

NASA CR.

140361

N75-13023

(NASA-CR-140361) THE HARD START
PHENOMENA IN HYPERGOLIC ENGINES. VOLUME
3: PHYSICAL AND COMBUSTION
CHARACTERISTICS OF ENGINE (Bureau of
Mines) 100 p HC \$4.75

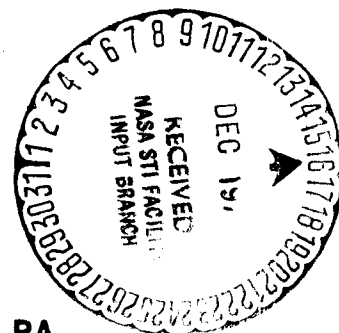
Unclass
CSCL 21H G3/20 04572

PITTSBURGH MINING AND SAFETY RESEARCH CENTER



THE HARD START PHENOMENA IN HYPERGOLIC ENGINES VOLUME III. PHYSICAL AND COMBUSTION CHARACTERISTICS OF ENGINE RESIDUES

Interim Report No. 1646
March 22, 1974



BUREAU OF MINES, PITTSBURGH, PA.

UNITED STATES
DEPARTMENT OF
THE INTERIOR

THE HARD START PHENOMENA IN HYPERGOLIC ENGINES

VOLUME III. PHYSICAL AND COMBUSTION CHARACTERISTICS
OF ENGINE RESIDUES

by

Yael Miron and H. E. Perlee

Prepared for
Manned Spacecraft Center
National Aeronautics and Space Administration
Houston, Texas
Order No. T-39882(G)

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

PITTSBURGH MINING AND SAFETY RESEARCH CENTER

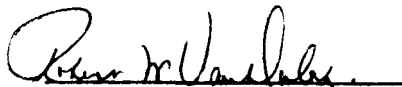
INTERIM REPORT NO. 1646

THE HARD START PHENOMENA IN HYPERGOLIC ENGINES
VOLUME III. PHYSICAL AND COMBUSTION CHARACTERISTICS
OF ENGINE RESIDUES

By

Yael Miron and H. E. Perlee

APPROVED:



Robert W. Van Dolah
Research Director
Pittsburgh Mining and
Safety Research Center

U.S. Department of the Interior
Bureau of Mines
Pittsburgh, Pennsylvania 15213
March 22, 1974

	<u>Page</u>
Introduction.....	7
Hydrazine nitrate (HN).....	11
Physical properties of HN.....	12
Crystalline forms and their melting points.....	12
Infrared and x-ray spectra.....	12
Mass loss rate of HN; dissociation and decomposition.....	14
Physical properties of multicomponent systems containing HN.....	21
Density of HN solutions with N_2H_4 and with water.....	21
Viscosity of HN solutions with N_2H_4 and with water.....	24
Surface tension of HN solutions with N_2H_4 and with water.....	24
Vapor pressure, heat of solution, and liquidus isotherms of HN/ N_2H_4 / H_2O solutions.....	30
Explosion characteristics of HN and its solutions.....	30
Thermal stability of HN.....	30
Detonation velocity of HN.....	32
Impact sensitivity of HN.....	34
Fast chemical reactions of HN.....	34
Explosion characteristics of systems containing HN.....	35
Thin-film detonation velocity.....	35
Detonation of thin-layer wall deposits of HN and HN solutions via gas-phase detonation.....	41
Detonation initiation by ethylene/oxygen detonation.....	41
Shock sensitivity of cavitated HN solutions.....	49
Gas-thin film detonation transition studies.....	53
Summary.....	61
Hydrazine dinitrate (H_2N).....	62
Introduction.....	62
Physical properties of H_2N	62
X-ray and infrared spectra.....	62
Dissociation and decomposition (weight loss rate).....	63
Chemical properties of H_2N	70
Reaction of H_2N with N_2H_4	70
Reaction of H_2N with NTO.....	73
Explosion characteristics of H_2N	73
TNT equivalence and impact sensitivity.....	73
Summary.....	73
Hydrazine nitrite.....	74
Introduction.....	74
Physical characteristics.....	74
Monomethylhydrazine nitrate (MN).....	76
Introduction.....	76
Physical properties of MN.....	76
Infrared and x-ray spectra.....	76
Thermal properties.....	79
Mass loss rate.....	79

	<u>Page</u>
Explosion characteristics of MN.....	79
Detonation behavior.....	79
TNT equivalence and impact sensitivity.....	83
Heating effects on MN.....	83
Formation of monomethylhydrazine dinitrate (M2N).....	83
Unsymmetrical dimethylhydrazine nitrate (UN).....	83
Introduction.....	83
Preparation and properties.....	85
Tetramethyltetrazene (TMT).....	87
Introduction.....	87
Physical characteristics.....	87
Explosion characteristics.....	90
Hydrazine azide.....	90
Introduction.....	90
Preparation and physical characteristics.....	90
Combustion characteristics.....	92
Nitrosyl azide.....	92
Summary.....	94
References.....	95

ILLUSTRATIONS

1. Infrared spectrum of HN.....	13
2. Infrared spectra of HN/N ₂ H ₄ solutions for: (a) A concentrated solution; and (b) a dilute solution.....	13
3. Quartz spring balance.....	16
4. HN weight loss at atmospheric pressure and at 227° C.....	17
5. HN weight loss rate as a function of temperature in the pressure range 300 to 500 μ Hg.....	18
6. HN weight loss rate as a function of pressure in the temperature range 230° to 240° C.....	19
7. Density of HN/hydrazine solutions at various HN concentrations as a function of temperature.....	22
8. Density of HN/water solutions at various HN concentrations as a function of temperature.....	23
9. Kinematic viscosity of HN/hydrazine solutions at various HN concentrations as a function of temperature.....	25
10. Kinematic viscosity of HN/water solutions at various HN concentrations as a function of temperature.....	26
11. Experimental apparatus used in the measurement of the surface tension of HN/N ₂ H ₄ and HN/H ₂ O solutions.....	27
12. Surface tension of HN/hydrazine solutions at various HN concentrations as a function of temperature.....	28
13. Surface tension of HN/water solutions at various HN concentrations as a function of temperature.....	29
14. Vapor pressure for water, hydrazine, and two HN/hydrazine solutions.....	31
15. Heats of solution of HN in water/hydrazine systems.....	31
16. Isotherms of the system HN/N ₂ H ₄ /H ₂ O.....	31

17. Detonation velocity of pressed HN as a function of density for various charge diameters.....	33
18. Thin-film detonation apparatus.....	36
19. Typical oscillograms of the pressure transducer and collapsible probe signals for: (a) Propagation of a stable detonation, and (b) no propagation.....	38
20. Detonable compositions of the ternary system HN/hydrazine/water.....	40
21. Test vessel for studying initiation of detonation in condensed explosives by gas-phase detonation.....	42
22. Apparatus used to study gas detonation initiation of condensed explosives.....	43
23. Surface pressure and continuous probe records for granular HN and NaCl samples.....	45
24. Initial reaction front velocity in granular HN as a function of initial gas mixture (25 pct C ₂ H ₄ /75 pct O ₂) pressure and theoretical gas detonation shock pressure.....	46
25. Test vessel fragmentation patterns following explosive (1-4) and nonexplosive (5) reactions.....	48
26. Apparatus to study the gas shock initiation of detonation in cavitated HN/N ₂ H ₄ solutions.....	50
27. Pressure record of cavitation experiment.....	52
28. Heterogeneous detonation apparatus.....	54
29. Gas-thin film studies; typical streak camera record.....	56
30. Shock mach numbers in gas-thin film studies.....	57
31. Shock mach numbers in gas-thin film studies.....	57
32. Shock mach numbers in gas-thin film studies.....	58
33. Shock mach numbers in gas-thin film studies.....	58
34. Shock mach numbers in gas-thin film studies.....	59
35. Infrared spectrum of H ₂ N.....	64
36. Weight loss of H ₂ N at 25° C and at 200 μ Hg.....	66
37. Weight loss of H ₂ N at 75° C and at 200 μ Hg.....	67
38. Percent initial weight loss rate of H ₂ N as a function of the reciprocal temperature at 200 μ Hg.....	69
39. Calorimeter used in the measurement of heat of reaction of H ₂ N with N ₂ H ₄	72
40. Infrared spectrum of hydrazine nitrite.....	75
41. Infrared spectrum of MN.....	77
42. Differential scanning calorimeter record of MN.....	80
43. A differential thermal analysis curve (thermogram) for residue from MMH/HNO ₃ reaction.....	81
44. A differential thermogram of MN.....	82
45. A differential thermogram of M ₂ N.....	84
46. Infrared spectrum of UN.....	86
47. Infrared spectrum of a dilute solution of UN in UDMH.....	86
48. Infrared spectrum of liquid TMT.....	89
49. Infrared spectrum of hydrazine azide.....	91

TABLES

	<u>Page</u>
1. Results of chemical analysis of Manned Spacecraft Center (MSC) residues.....	9
2. X-ray diffraction spectrum for HN.....	12
3. X-ray diffraction spectrum for HN.....	14
4. Detonation velocities and critical film thicknesses (CFT) of both low- and high-velocity detonations of molten HN, HN-water, and HN-hydrazine solutions at 75° C.....	37
5. Calculated constant volume explosion characteristics of condensed phase HN/N ₂ H ₄ mixtures.....	37
6. Reaction pressures and propagation velocities in granular HN initiated by a C ₂ H ₄ /O ₂ gas detonation.....	47
7. Calculated detonation pressure ratios for various N ₂ H ₄ /NTO gas mixtures at an initial pressure of 1 atm.....	53
8. X-ray diffraction spectrum of H ₂ N.....	63
9. Decomposition of H ₂ N; summary of results.....	68
10. X-ray diffraction spectrum of UN.....	78
11. X-ray diffraction spectrum of MN.....	87
12. Mass spectrum of TMT.....	88
13. X-ray diffraction spectrum of hydrazine azide.....	92

THE HARD START PHENOMENA IN HYPERGOLIC ENGINES

VOLUME III. PHYSICAL AND COMBUSTION CHARACTERISTICS
OF ENGINE RESIDUES

by

Yael Miron¹ and H. E. Perlee²

INTRODUCTION

Many causes have been suggested for the occasional destructive ignition of the Apollo Reaction Control (RSC) engines under simulated high-altitude conditions. One of these concerned the formation of explosive substances or mixtures, during the preignition and postcombustion periods of engine operation. None of the known destructive ignitions reportedly occurred on the first firing of a clean engine. This observation seemed to substantiate the suggestion that explosive substances accumulated in the engine during the subsequent firings, occasionally reaching proportions sufficient to damage the engine when they were ignited. It has also been suspected that propellants leaking into the very low pressure engine environment, as it is in deep space, due to faulty valve operation, can also react to form explosive substances. The potentially explosive materials that are suspected and identified in the nonflame reactions include the mononitrates and dinitrates, the mononitrites and dinitrites, and azides of hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine; the hydrogen azide, nitrosyl azide, ammonium azide, and ammonium nitrate. To evaluate the credibility of this suggested source of the RCS engine hard-start problem, as it is termed, it was necessary to:

1. Establish that chemical reactions occurred during the preignition and postcombustion periods.
2. Identify the chemical species of the products of preignition and postcombustion reactions.
3. Determine the explosive nature of the identified species.

Indeed, it has been found by the Bureau and by other investigators, that the various substances mentioned above are formed during preignition and postcombustion periods. Their formation and identification in engine residues, in prototype-engine reaction products, and in gas-phase and liquid-phase reactions in various experimental setups are described and discussed in volume IV of this report.

¹Chemical research engineer.²Chief, Theoretical Support

Both authors are with the Pittsburgh Mining and Safety Research Center, Bureau of Mines, U.S. Department of the Interior, Pittsburgh, Pa.

Once this fact that these materials form and are present in the engine has been established, as it is in volume IV, it becomes important to determine the explosive nature of these materials.

In order to be able to study the combustion properties, the various substances had to be prepared in sufficient quantity and at high purity. Since, at the time of this investigation, methods of preparation and identification (i.e., infrared spectra, x-ray spectra, and so forth) of many of these materials were not available in the literature, the methods used by the Bureau are briefly described here. Also given are the infrared spectra, x-ray spectra, and/or any other signatures of the compounds, obtained both by Bureau investigators and by others. Thus, this volume contains all the available information pertaining to the physical and explosion characteristics of hydrazine nitrate (HN), monomethylhydrazine nitrate (MN), unsymmetrical dimethylhydrazine nitrate (UN), hydrazine dinitrate (H₂N), hydrazine nitrite, tetramethyltetrazene (TMT), hydrazine azide, and nitrosyl azide.

At this point, it is interesting to note the results of the analyses of residue material collected by Manned Spacecraft Center (MSC) personnel, following engine shutdown, from various locations in the environmental test chamber and from the RCS rocket engine which are presented in table 1. The fuel used in these tests was Aerozine-50 (or A-50, a 50:50 mixture of hydrazine and unsymmetrical dimethylhydrazine). HN was detected in most of the residues examined.

TABLE 1. - Results of chemical analysis of Manned
Spacecraft Center (MSC) residues

Sample No.	Origin of MSC sample	Residue/ distillate	Distillate composition (analyzed by GLC) ¹		Residue composition (infrared analysis)
		Weight ratio	Constituent	Mole, pct	Weight pct
10	Rocket nozzle.....	² 100/0	-	-	HN >90
12	Environmental chamber wall.....	58/42	Water Hydrazine Unknown	95 0 5	HN >90
13	Cooling shroud.....	7/93	Water Hydrazine Unknown	98 0 2	Not enough residue recovered for reliable analysis
14	Rocket combustion chamber.....	² 100/0	-	-	HN >90
16	Injector face following run No. 59-22.....	² 100/0	-	-	HN >90
19	Residue taken July 22, 1966 after 1,000 pulses; origin unknown.....	² 100/0	-	-	HN >90
24	Precup (after block 74) ³	29/71	Water Hydrazine UDMH	93.0 4.5 2.5	HN >90 (Possible ammonium nitrate)

¹GLC: Gas-liquid partition chromatography.

²Sample received as solid.

³MSC test run designation.

The residues collected in experimental engines, flow reactors, and other test configurations by various researchers, including the Bureau, consisted mainly of dilute solutions of nitrate salts in water and unreacted fuel or of solutions of nitrate salts in water and unreacted oxidant. Other substances were found in these residues in small quantities. The type of salt formed depended on the fuel used.

A point that must be stressed here is the observation by the Bureau that the concentration of salts in the residues depended on the sampling time. At times, if the products on the two-dimensional (2-D) experimental engine walls, for example, were not collected immediately, they adsorbed water. This could be observed visually by the paling of the light-yellow color of the residue solution, by the increase in the volume of the thin films of residue on the walls, and by the change in the infrared spectrum of the sample when collected at different sampling times. At other times (probably dependent, among other factors, on temperature and humidity at time of sampling), thin powdery layers and even very fine crystals were found on the walls of the 2-D engine and gas flow reactor, which were originally covered with a thin layer of liquid. Of course, as soon as these were exposed to a humid atmosphere, they adsorbed water. There is no way of determining the concentration of the various salts in the residue when explosions did occur in the RCS engines. The residues that were examined were always those taken from the walls when explosions did not take place; it is presumed that they may lead to explosions. For this reason, the combustion characteristics of the pure nitrate salts as well as of the concentrated and dilute solutions of the salts were evaluated.

Two methods of residue analysis and identification were used. In the first method, one compared the spectra of the residues with available spectra of the aqueous solutions of the various nitrate salts and of the salts in their liquid propellant precursors (i.e., HN in hydrazine). The other method was via separation and purification, followed by chemical and physical analysis of the residue contents. For this purpose, melting points, boiling points, crystal structure, and other physical properties are needed.

Not only was it necessary to identify the residues and to determine their potential hazards, but methods for their removal from the engine walls were also considered. An obvious removal technique would be to evaporate the residues; this would require cyclic heating of the engine walls. In order to assess the possibilities of this method, i.e., the maximum temperature, and length of heating period needed, the evaporation rates, at different temperature and pressure conditions, and the evaporation made had to be measured. Evaporation or mass loss rates of HN, one of the major compounds found in engine residues, are reported in some detail here. The results of this study indicated that complete removal of residues containing HN by evaporation, in a reasonable time and using reasonable temperatures, was not feasible. Mass loss rates of H₂N and of MN were also measured, though not in as much detail as for the HN. The latter two materials evaporate at much higher rates than does HN; also, both materials are less sensitive explosives.

Properties such as surface tension, viscosity, and density, although not of direct interest to the problem of explosive ignitions in the RCS engines, can indirectly affect residue removal or possibly even thin-layer detonation. For this reason, the surface tension, viscosity, and density of aqueous solutions of HN and of hydrazine solutions of HN were measured and are reported here.

Much emphasis has been placed on HN and its solutions, as is evident in this volume. This is due to the fact that HN was among the first compounds to be identified in the engine residues; it is found more often than are other compounds in engine residues from runs in which the fuel was either N_2H_4 or A-50 (the latter being used more often than the other fuels), also because it was found to be a more sensitive explosive. UN, on the other hand, was found to be sensitive to heat and easily converted to ammonium nitrate; it was seldom found as a constituent of residues in engine and flow reactor tests.

A final section in the section on HN deals with an investigation of the significance of cavitation on detonability of HN/hydrazine solutions and with the initiation of detonation in thin films of this solution by gas detonation.

HYDRAZINE NITRATE (HN)

Hydrazine nitrate (HN) was first prepared in 1889 by Curtius and Jay (1).³ HN exists in two crystalline forms, α and β . The β form is metastable and, except for the melting point, little is known about it. The data presented in this volume concern only the α form. HN used in the Bureau studies was prepared according to a procedure recommended by the Thiokol Corporation (2), in the following manner: Commercial anhydrous hydrazine was dissolved in methanol and cooled to $-20^\circ C$. Concentrated nitric acid, also at $-20^\circ C$, was then added drop-wise to the hydrazine-methanol solution, while carefully maintaining the temperature below $0^\circ C$, until a pH of 5.5 was reached. The white crystalline HN precipitated during the addition process is filtered off, melted in boiling methanol, and recrystallized. This recrystallization is repeated twice more. Following filtration, the last trace of methanol is removed in vacuum and the purified salt is dried and stored in a desiccator over phosphorous pentoxide. Chemical analysis of the prepared crystals was done by the nitron-nitrate precipitation technique (3). This same technique was used for analysis of all the other nitrate salts.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Physical Properties of HN

Crystalline Forms and Their Melting Points

The stable, α crystalline form of HN, with a crystal density of 1.661 grams/cm³, melts at approximately 70° C with no apparent decomposition or sublimation. The metastable β form melts at 62° C. Robinson and McCrone (4) found that a melt of HN supercools readily and usually crystallizes as the metastable β form. Sommer (5) noted that HN exhibits monotropism, i.e., the β form always converts to the α form with the evolution of heat. Using differential scanning calorimetric (DSC) techniques, the Bureau obtained a value of 2.0 Kcal/mole for the heat of conversion of the β to the α form. No additional thermal phase changes in the crystalline structure of the α form were found from -70° C to the melting point.

Infrared and X-ray Spectra

The infrared absorption spectra of HN and of HN/hydrazine (N₂H₄) solutions obtained by the Bureau are shown in figures 1 and 2, respectively. The x-ray diffraction spectrum obtained by the Bureau is shown in table 2, while that obtained by Robinson and McCrone (4) is shown in table 3.

TABLE 2. - X-ray diffraction spectrum for HN¹

$d, \text{\AA}$	I/I_0	$d, \text{\AA}$	I/I_0
4.42	20.6	2.10	8.6
3.98	80.2	2.05	22.2
3.59	27.2	1.91	27.7
3.25	100.0	1.87	13.8
2.89	17.8	1.68	12.7
2.69	59.5	1.52	9.9
2.40	33.2	1.42	17.6
2.34	9.2	1.39	1.39
2.24	23.9	1.37	1.37

¹Results obtained by Bureau investigators.

I/I_0 = ratio of scattered-to-incident beam intensities.

D = wavelength of the scattered line.

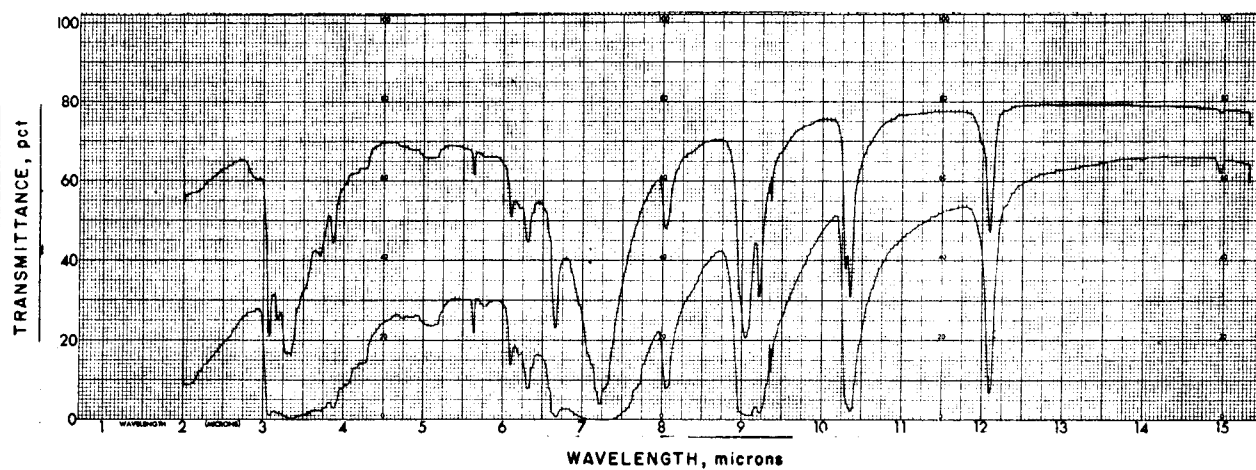


FIGURE 1. - Infrared Spectrum of HN.

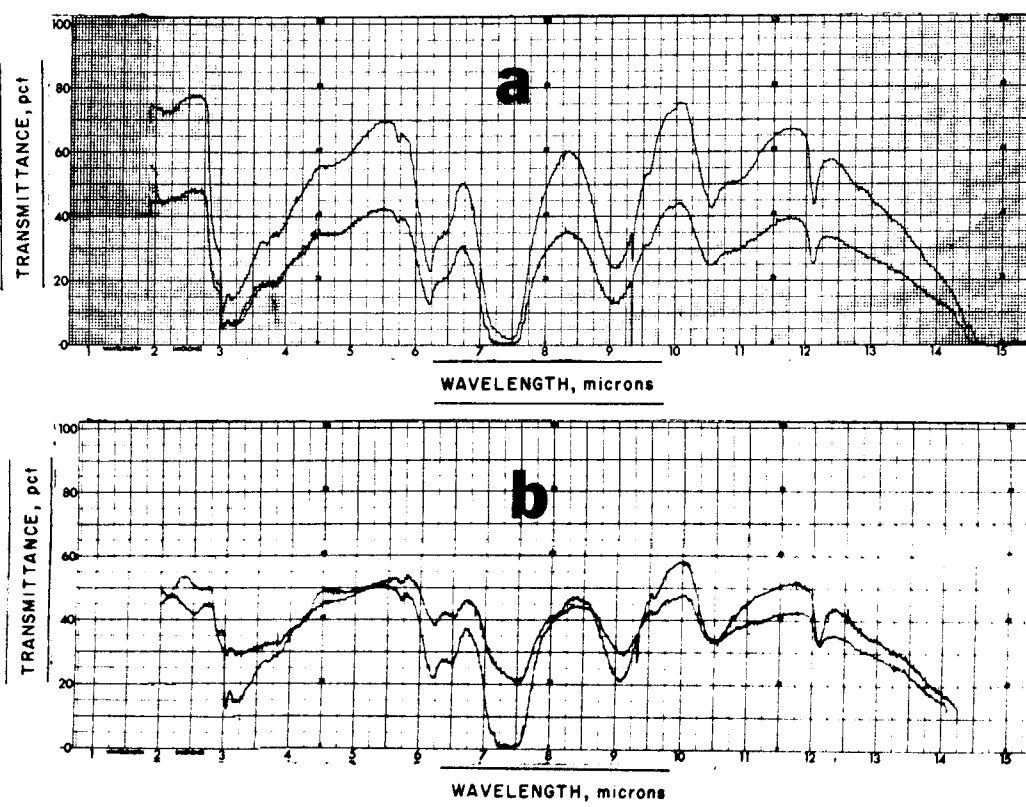


FIGURE 2. - Infrared Spectra of HN/N₂H₄ Solutions for:
 (a) A Concentrated Solution; and (b) A Dilute Solution.

TABLE 3. - X-ray diffraction spectrum for HN¹

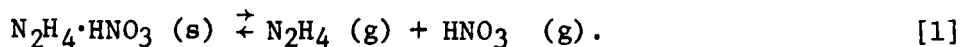
d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀
5.85	10	2.42	20	1.597	3	1.121	1
5.62	70	2.38	70	1.559	1	1.102	1
4.68	50	2.34	10	1.530	5	1.084	1
4.10	80	2.26	40	1.463	2	1.066	1
3.34	100	2.12	30	1.439	2	0.9616	1
3.20	10	2.05	60	1.418	4		
3.11	50	1.999	10	1.386	2		
3.03	30	1.951	40	1.350	2		
2.93	40	1.925	40	1.308	1		
2.87	40	1.884	40	1.253	1		
2.81	20	1.864	20	1.253	1		
2.70	90	1.772	40	1.227	1		
2.61	30	1.749	20	1.207	1		
2.58	70	1.691	40	1.164	1		
2.52	40	1.658	10	1.150	1		
2.46	30	1.615	30	1.134	1		

¹This data were obtained by Robinson and McCrone (4).

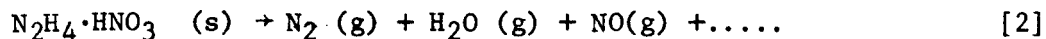
The nitrate ion has four fundamental modes of vibration, all of which are observable in the infrared, but only two are normally sufficiently intense to be used for identification purposes. These are the two at 1,390 cm⁻¹ (7.2 μ) and 800 cm⁻¹ (12.5 μ).

Mass Loss Rate of HN; Dissociation and Decomposition

Ionic materials such as HN undergo two types of mass loss phenomena. One is dissociation, in which HN molecules dissociate into N₂H₄ and HNO₃ vapor species according to the reaction,



These vapor species recombine, upon cooling, in a process of reverse sublimation to form the original solid HN. The other process of mass loss is decomposition, in which the HN molecule breaks apart, and is supposedly represented by the expression,



The resultant gaseous species do not recombine upon cooling to form the original HN.

Medard (6) determined the weight or mass loss of anhydrous HN during intermittent heating to 110° C for 315 hours and found that it was linearly time-dependent and about 8 x 10⁻⁵ weight percent per minute. Kissinger (7)

used standard vacuum stability techniques and did not detect any decomposition at 140° C. Sabanejeff (8) found weight loss rates of 0.003 and 0.09 weight percent per minute at 145° and 215° C, respectively.

Cook and Abegg (9) measured the rate of the isothermal weight loss of HN in a quartz spring balance facility, at various temperatures, and found that their results fitted an Arrhenius relationship as follows:

$$K(T) = 10^{12.2} \cdot e^{-\frac{38,000}{RT}} \quad [3]$$

where $K(T)$ = specific reaction rate constant, Sec.^{-1} .

The Bureau measured mass loss rates of HN in two types of apparatus, the DSC and a quartz spring balance in a controlled temperature and pressure environment. The spring balance is illustrated in figure 3.

Small samples weighing approximately 20 mg and with an initial surface area of 0.2 cm² were examined at various temperatures, both below and above the melting point (70° C) in the DSC, in which the pressure was atmospheric. Experiments conducted at temperatures below the melting point showed no perceptible weight loss over a 48-hour period. At temperatures above melting, weight loss varied linearly with time; at 150° C it was 0.006 weight percent per minute, at 200° C it was 0.04 weight percent per minute, and at 250° C it was approximately 3 weight percent per minute. Since precise pressure conditions and exposed molten surface areas were not known, comparison of results of the various studies was pointless; nonetheless, in general, results are of the same order of magnitude and follow the right trend of increasing loss rate with increasing temperature.

Somewhat more detailed experiments in which the pressure, temperature, and the apparent surface area of the sample were known, were made by the Bureau in the quartz spring balance. In order to simulate vaporization processes as they occur in the RCS engines in a deep-space environment, most of the experiments were conducted at pressures lower than 1 mm Hg. Typical results of these experiments at various conditions are shown in figures 4 and 5. Figure 4 shows typical results at atmospheric pressure and 226° and 228° C for a 1-gram sample. The initially large rate indicates initial loss of water or methanol after which the slope of the curve changes to that of the HN mass loss rate. Figure 5 shows the mass loss rate of HN at various temperatures for an average pressure of 300 to 500 μ Hg. Figure 6 shows the mass loss rate at an average temperature of 230° to 240° C for various pressures, and it can be seen that the evaporation process is sensitive to pressure. Above 250° C, the thermal process becomes unstable and the HN decomposes explosively.

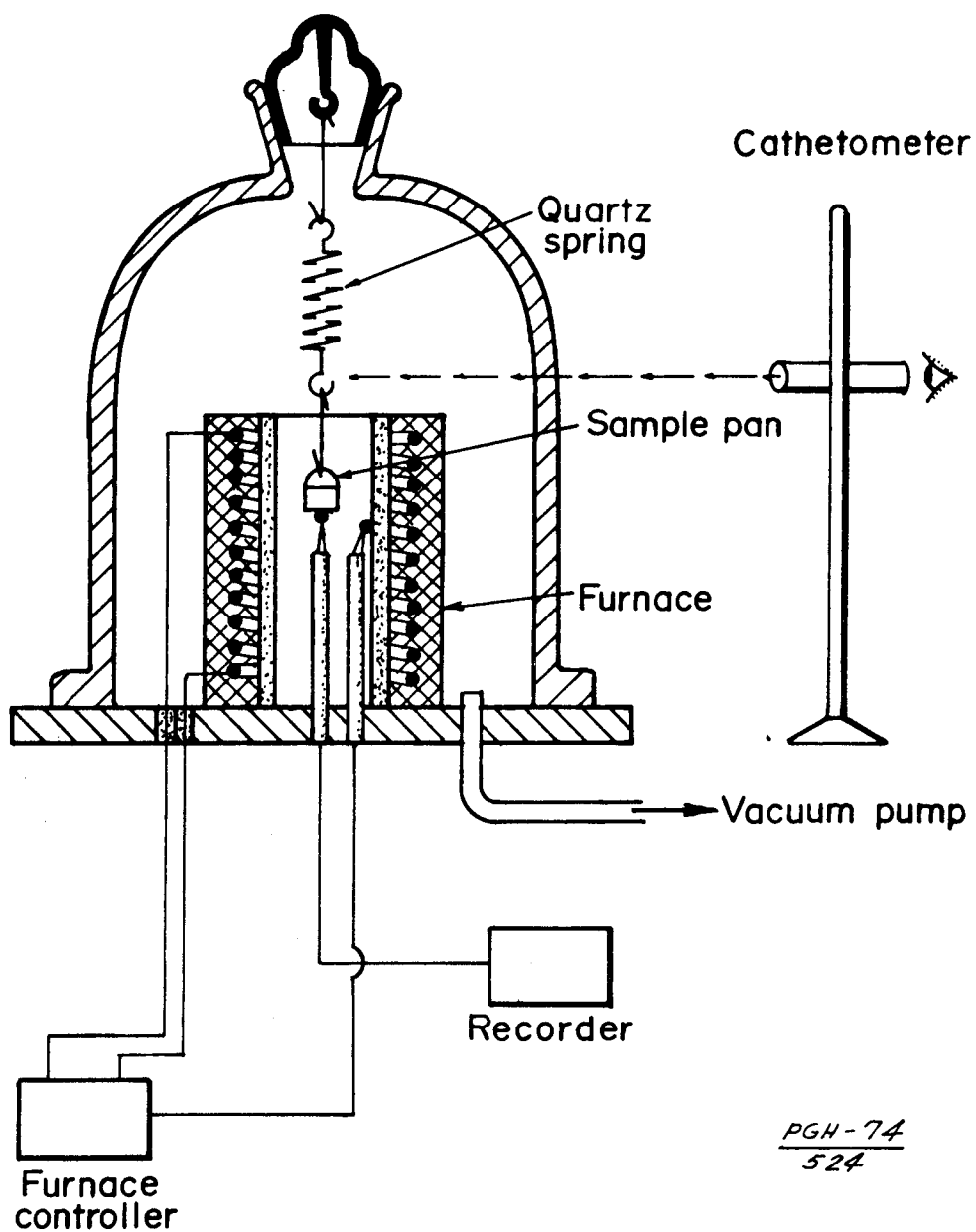
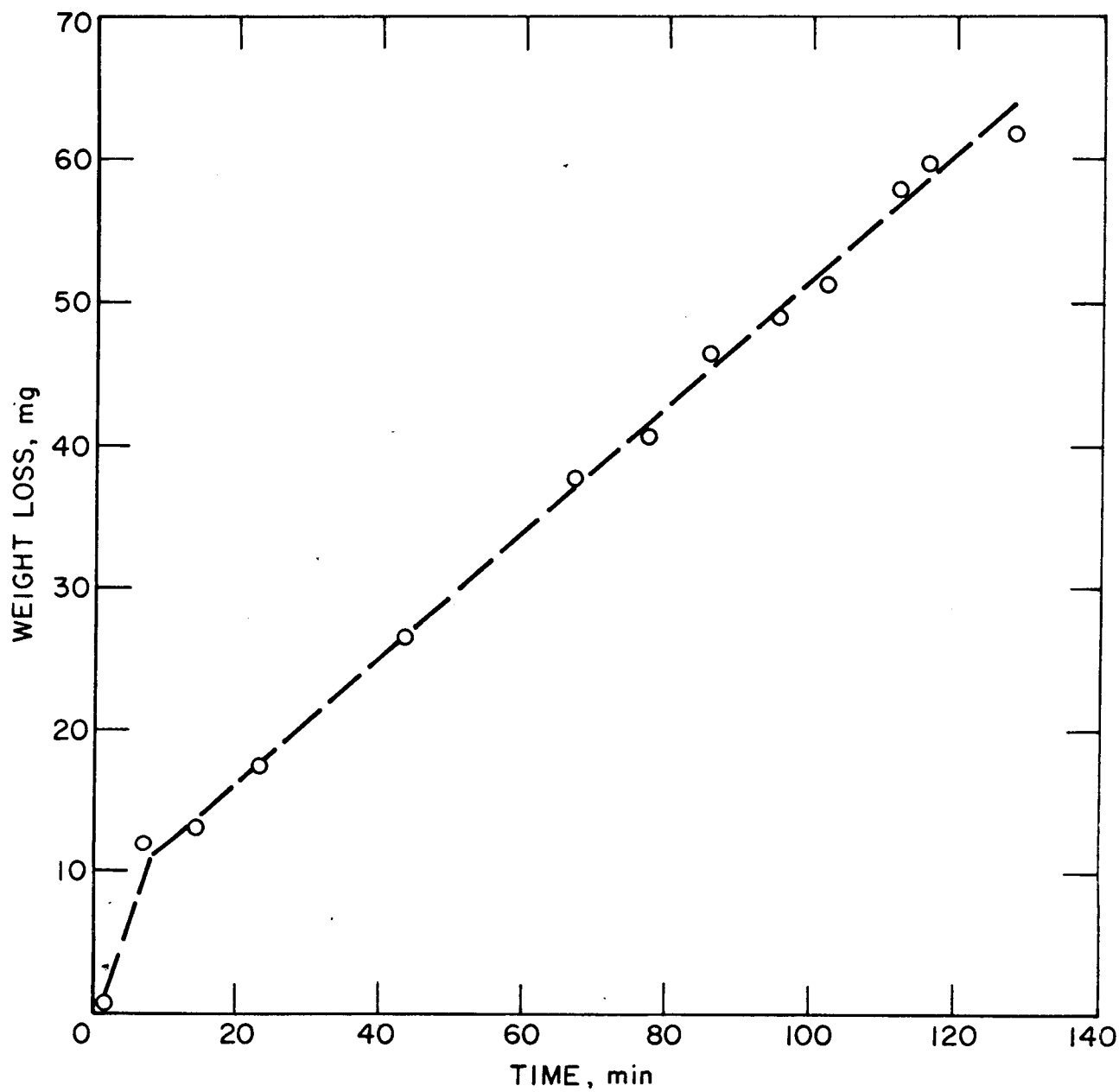
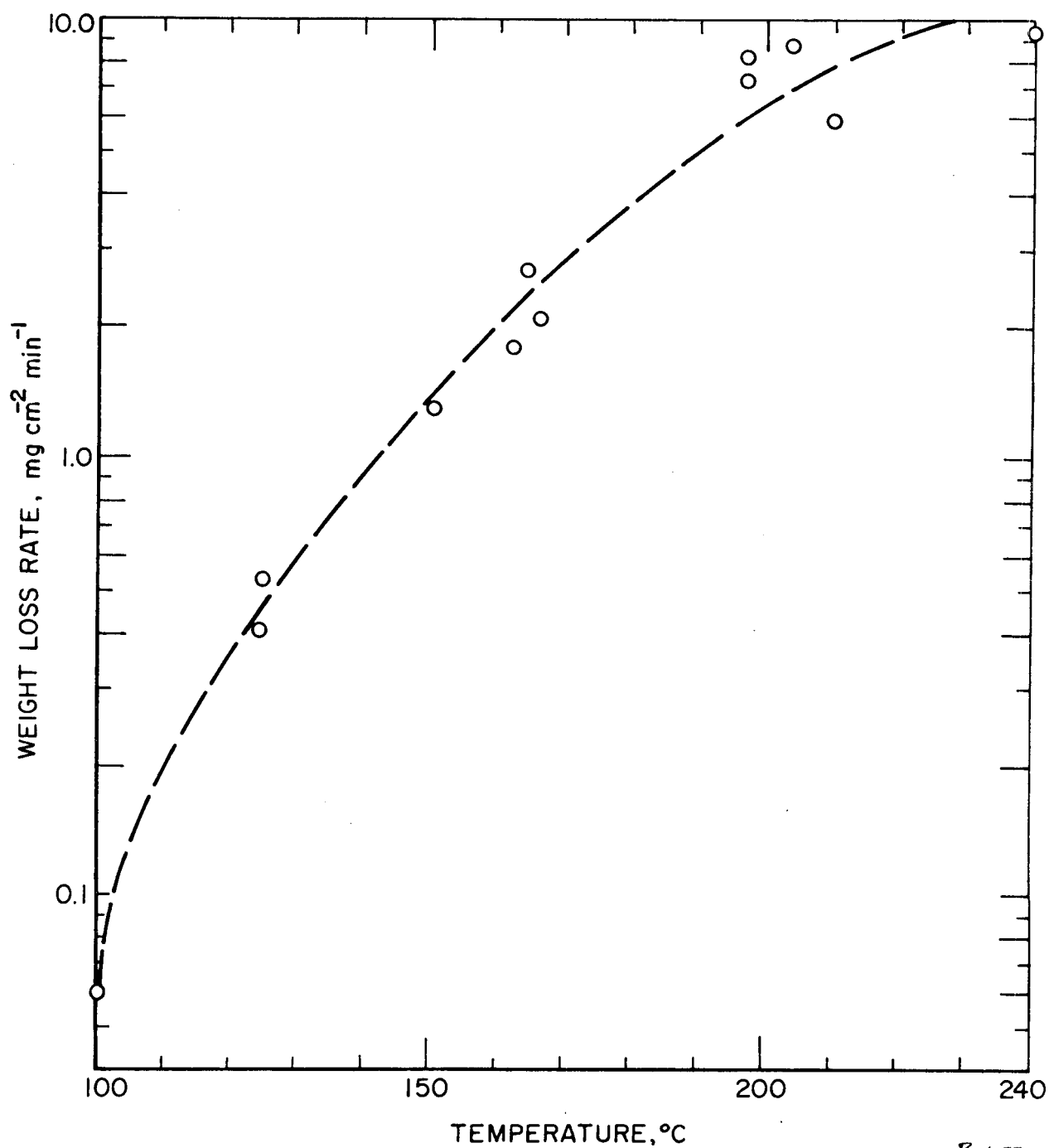


FIGURE 3. - Quartz Spring Balance



P64-73
382

FIGURE 4. - HN Weight Loss at Atmospheric Pressure and at 227° C.



PGH-73
381

FIGURE 5. - HN Weight Loss Rate as a Function of Temperature in the Pressure Range 300 to 500 μ Hg.

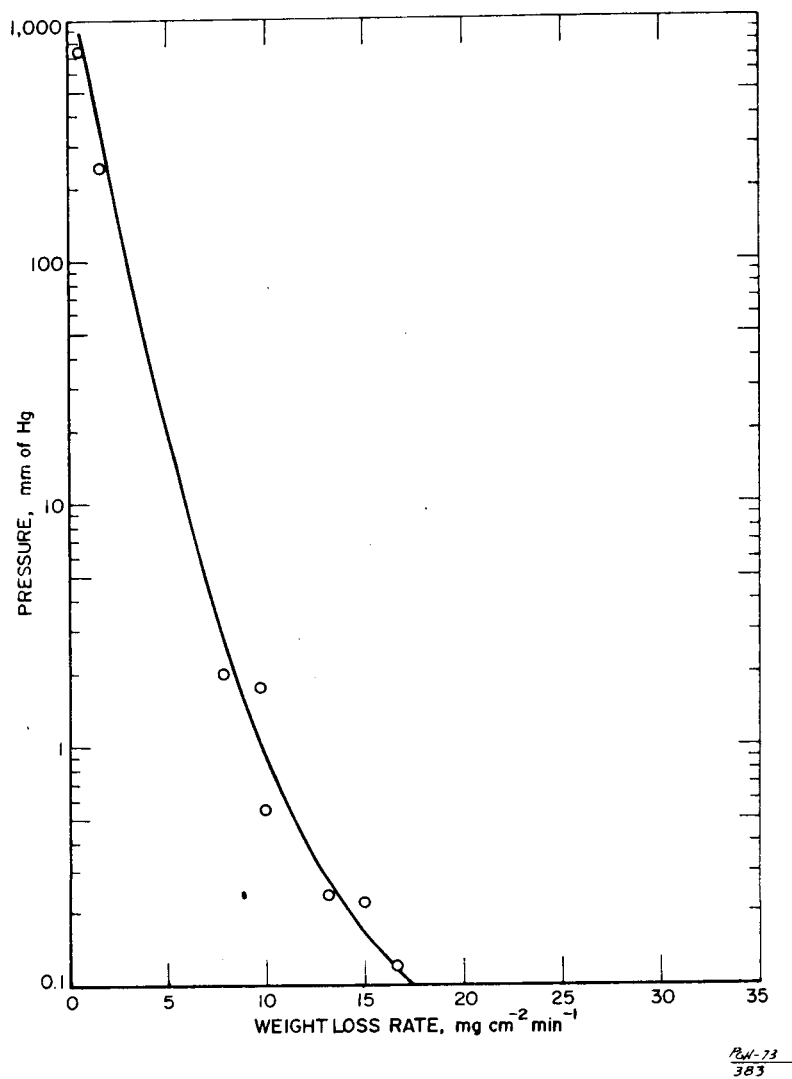


FIGURE 6. - HN Weight Loss Rate as a Function of Pressure in the Temperature Range 230° to 240° C.

At temperatures below 150° C, samples boiled gently and the surface of the sample corresponded closely to the cross-sectional area of the quartz pan containing the molten HN; at higher temperatures, boiling was vigorous and the exposed sample surface became poorly defined. This resulted in considerable uncertainty in calculating mass loss rate per unit surface area; however, for calculation purposes, the apparent pan-surface area was used. Since the same phenomenon will occur on the engine walls, given the same conditions, these experimental results are satisfactory for evaluating the time needed to remove residue layers from the walls.

It is assumed, for the purpose of the calculations, that water and unreacted fuel boil off first, leaving behind a layer rich in HN. Although the HN used in the Bureau experiments was purified and dried with considerable care, small amounts (<1 pct) of water and methanol could still be found and it is believed that these more volatile materials contribute to the initially large mass loss rate often observed in these experiments.

In both sets of experiments, the reversibly-sublimated or recombined vapor products of the evaporated HN deposited on cold areas inside the test apparatus. These deposits were collected and analyzed both qualitatively and quantitatively, and were found to constitute over 99 pct of the original sample weight loss, and to be indeed HN. This was true even at the high temperature of 240° C. This indicates that the evaporation of HN at temperatures up to 240° C and at pressures below atmospheric can be attributed entirely to dissociation processes. Ammonium nitrate similarly dissociates at low pressures, although at atmospheric pressure it decomposes.

Using the results from the latter experiments (spring balance), one can calculate the time necessary to evaporate a thin continuous layer of molten HN, 1 mil thick at 500 microns Hg pressure for various engine wall temperatures, and compare the resultant rate of removal with the rate of formation of HN in the engine to determine if thermal evaporation can eliminate the HN residue in the short periods between engine pulses. The calculated times needed for removal of HN by heating at different temperatures are as follows.

Temper- ature, ° C	Time for complete evaporation
72	30 min
135	3 min
175	1 min
240	10 sec

At lower pressures which are found in actual space flight the time required will be shorter; but it is suspected that even at very low pressure the needed time will be much too long for actual engine operation. The experiments reported in volume IV show that during the preignition period alone these engines produce HN at a rate of approximately 10 mg per pulse, or for 30 pulses per second, 300 mg per second. These 300 mg will form a layer 0.85 mil thick on the internal surface of the engine of approximately 85 sq in. To remove the HN at this corresponding rate would require temperatures in excess of 250° C, which is undesirable because of the known explosive decomposition of HN at these temperatures. Thus, the thermal removal of HN residues formed during preignition by means of thermal evaporation does not seem feasible. The problem is even more acute regarding residues formed during postcombustion. It is believed that because of the large void volume of the RCS engine fuel injector manifold, the greatest proportion of the HN residue is formed during this postcombustion period. This formation has been observed in NASA photographic film records of tests in plastic engines. Estimated amounts of residues that formed in the engine during this period were of the order of 10 grams per second.

In summary, if HN residues are the major cause of explosive ignitions in the engines, and if a desirable solution to this problem is the fast removal of the residues from the engine, it would appear that thermal dissociation will not constitute a satisfactory method.

Physical Properties of Multicomponent Systems Containing HN

Density of HN Solutions with N_2H_4 and with Water

The density of HN/ N_2H_4 and HN/water solutions at various temperatures and HN concentrations was determined by the Bureau as well as by other researchers. Figures 7 and 8 show the results obtained by the Bureau. Regression analysis of these data show that the densities of these solutions, ranging in concentration from 10 to 75 weight percent of HN and at temperatures ranging from 25° to 100° C, can be adequately described by the relation,

$$\rho = \rho_0 + aN + bN^{1/2}, \quad [4]$$

in which ρ and ρ_0 are the densities of the solution and solvent in grams/cm³, respectively, at the same temperature, N is the normality of the solution, and a and b are regression coefficients. For the HN/hydrazine solutions, a and b equal 0.027 and 0.032, respectively, and 0.030 and 0.018, respectively for HN/water solutions.

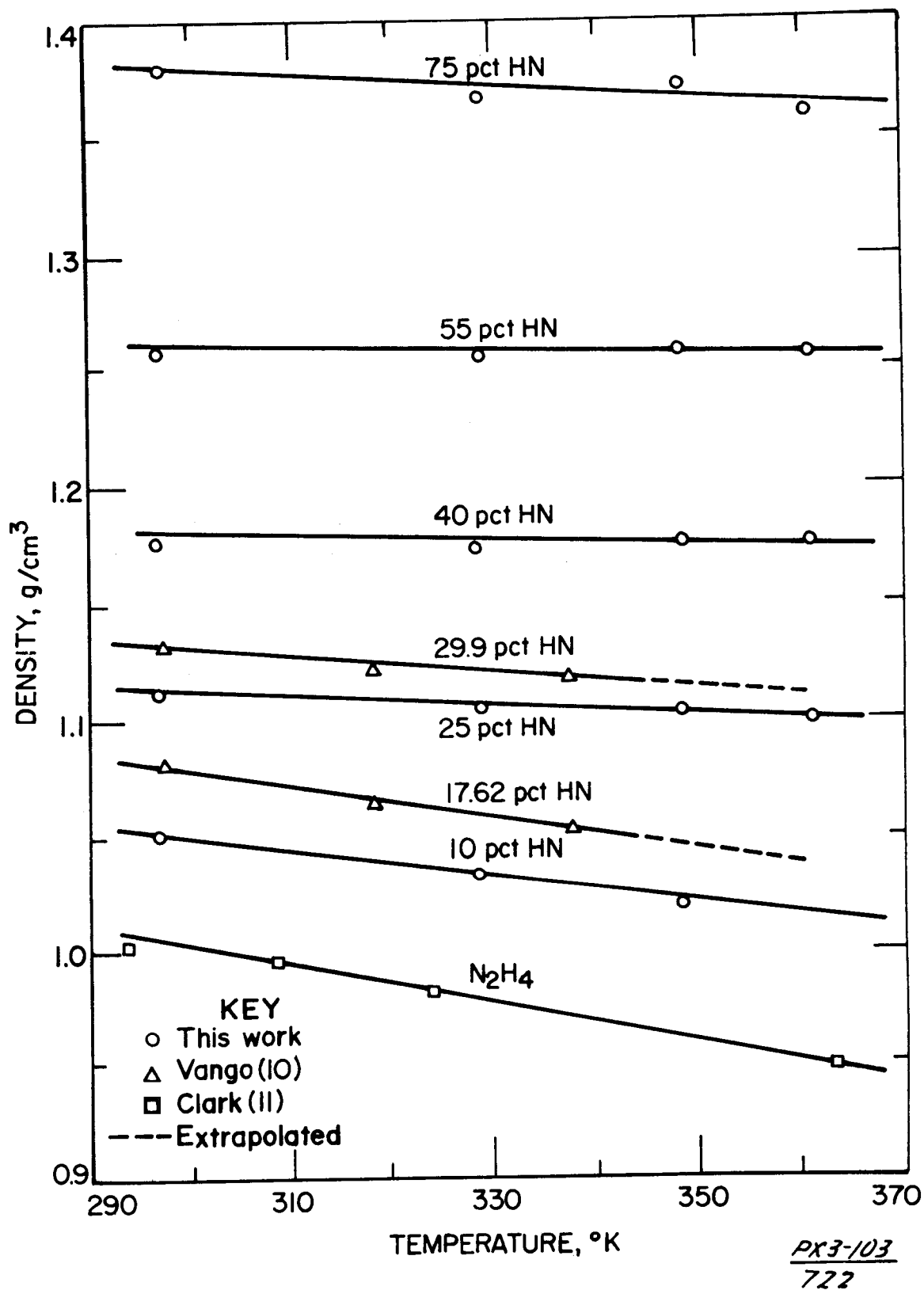


FIGURE 7. - Density of HN/Hydrazine Solutions at Various HN Concentrations as a Function of Temperature.

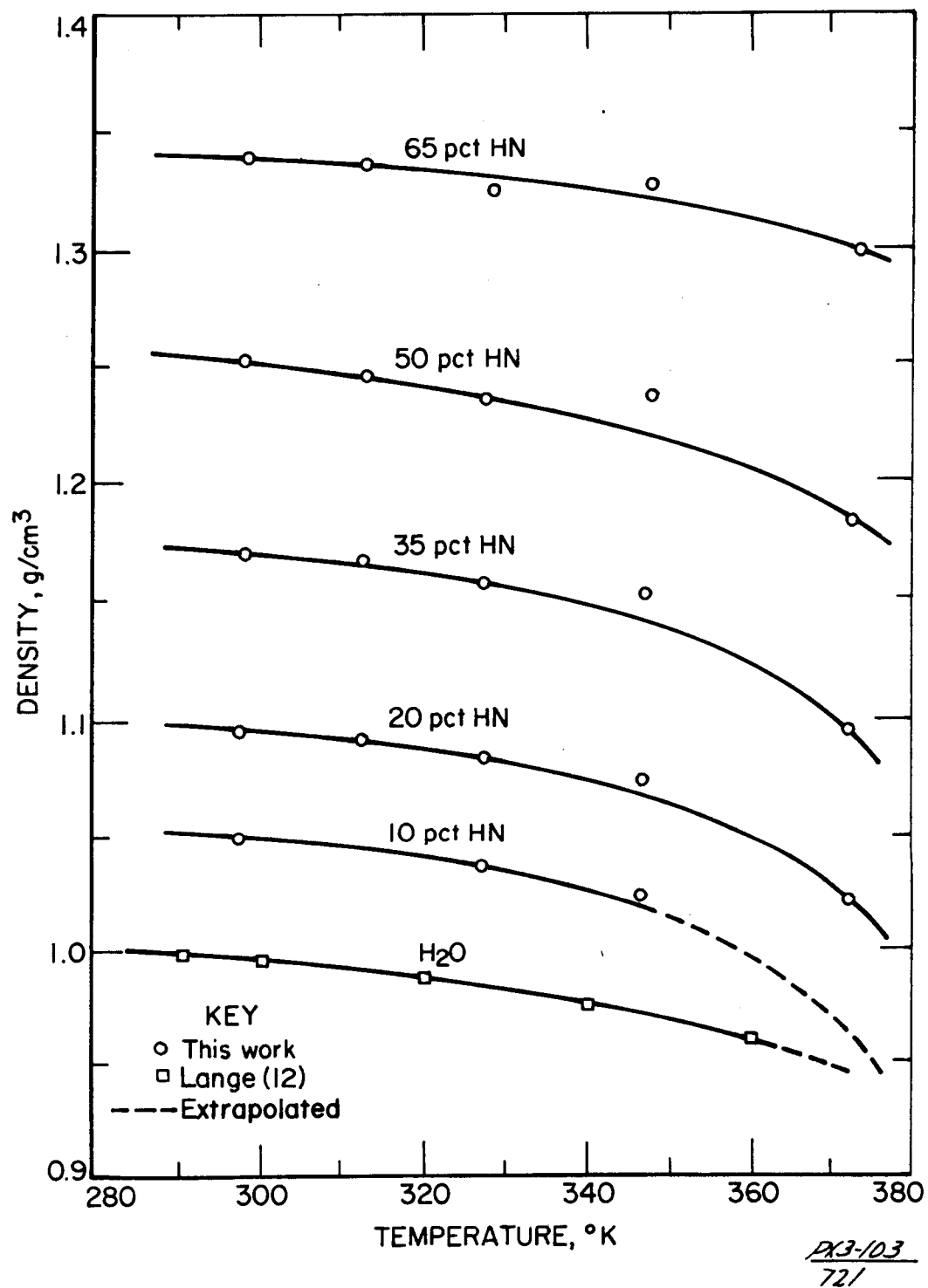


FIGURE 8. - Density of HN/Water Solutions at Various HN Concentrations as a Function of Temperature.

Vango and Krasinsky (10) measured the density of two HN/hydrazine solutions containing about 0.3 weight percent aniline as a function of temperature. Of the two solutions tested, one contained 17.62 weight percent and the other contained 29.97 weight percent HN. Figure 7 includes a plot of Vango and Krasinsky's (10) results; for comparison, the temperature dependence of the density of pure hydrazine taken from the work of Clark (11), and of water taken from Lange (12) is shown in figures 7 and 8, respectively.

Viscosity of HN Solutions with N_2H_4 and with Water

The kinematic viscosity of molten HN and of various HN/ N_2H_4 and HN/water solutions as a function of temperature and HN concentration was measured with a Cannon-Fenske viscometer. The results are shown in figures 9 and 10. The viscosities of hydrazine and water, in the same temperature range, are included for comparison. Regression analysis of the viscosity data for HN/hydrazine solutions gave the relation,

$$\log_{10} \frac{\nu}{\nu_0} = K \frac{N}{T}, \quad [5]$$

in which ν and ν_0 are the kinematic viscosities in centistokes of the solution and solvent, respectively, at absolute temperature T , in degrees Kelvin; N is the solution normality, and K is a regression coefficient equal to 24.59, in degrees Kelvin. In the case of HN/water solutions, regression analysis of the data yielded the expression,

$$\log_{10} \frac{\nu}{\nu_0} = K \frac{N^2}{T}, \quad [6]$$

in which K is 1.25, in degrees Kelvin. For comparison, figure 9 shows also the results obtained by Vango and Krasinsky (10) for two HN/hydrazine solutions using a Cannon-Zhukov viscometer. There is good agreement between the results obtained by Vango and Krasinsky (10) and by the Bureau.

Surface Tension of HN Solutions with N_2H_4 and with Water

The Bureau also determined the surface tension of various HN/ N_2H_4 and HN/water solutions at different temperatures. The bubble pressure method described by Partington (13) was used because surface contamination effects are minimized by this method. Figure 11 shows the experimental setup. The surface tension of molten HN and various HN/ N_2H_4 and HN/water solutions at elevated temperatures were measured; the results are shown in figures 12 and 13. Regression analysis of these data shows that the surface tension can be adequately described by the expression,

$$\gamma = \gamma_0 + (K_1 C - K_2)(T - T_0), \quad [7]$$

in which γ and γ_0 are the surface tensions in dynes per centimeter of the solution and solvent, respectively, at absolute Kelvin temperatures T and T_0 , respectively; C is the HN concentration in mole-percent, and K_1 and K_2 are regression coefficients (in dynes per centimeter per $^\circ K$). For HN/hydrazine solutions, γ_0 , T_0 , K_1 , and K_2 equal 93.82, 213.58, 0.302, and 0.243, respectively, and for HN/water solutions, γ_0 , T_0 , K_1 , and K_2 equal 92.69, 229.45, 0.220, and 0.248, respectively.

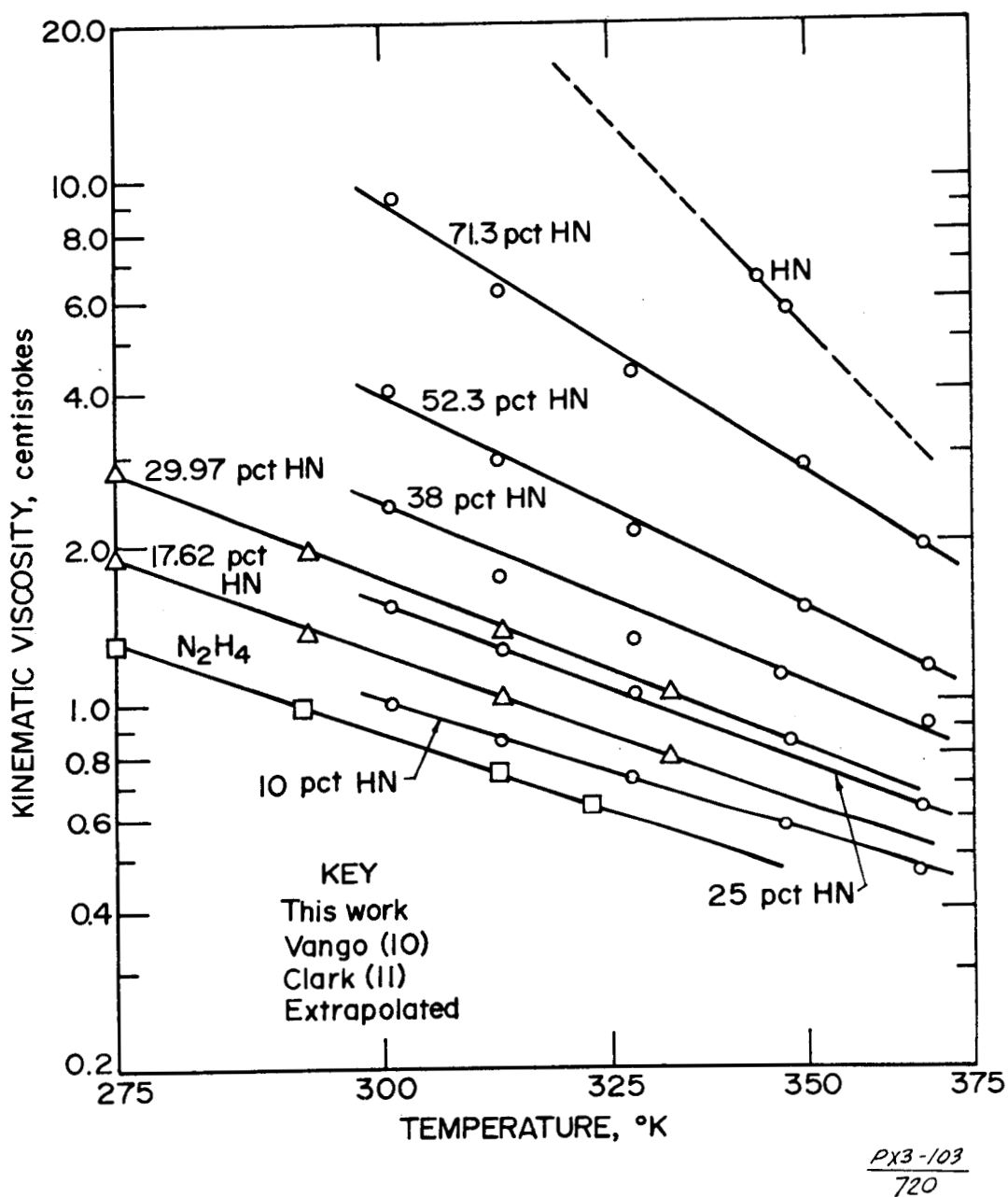
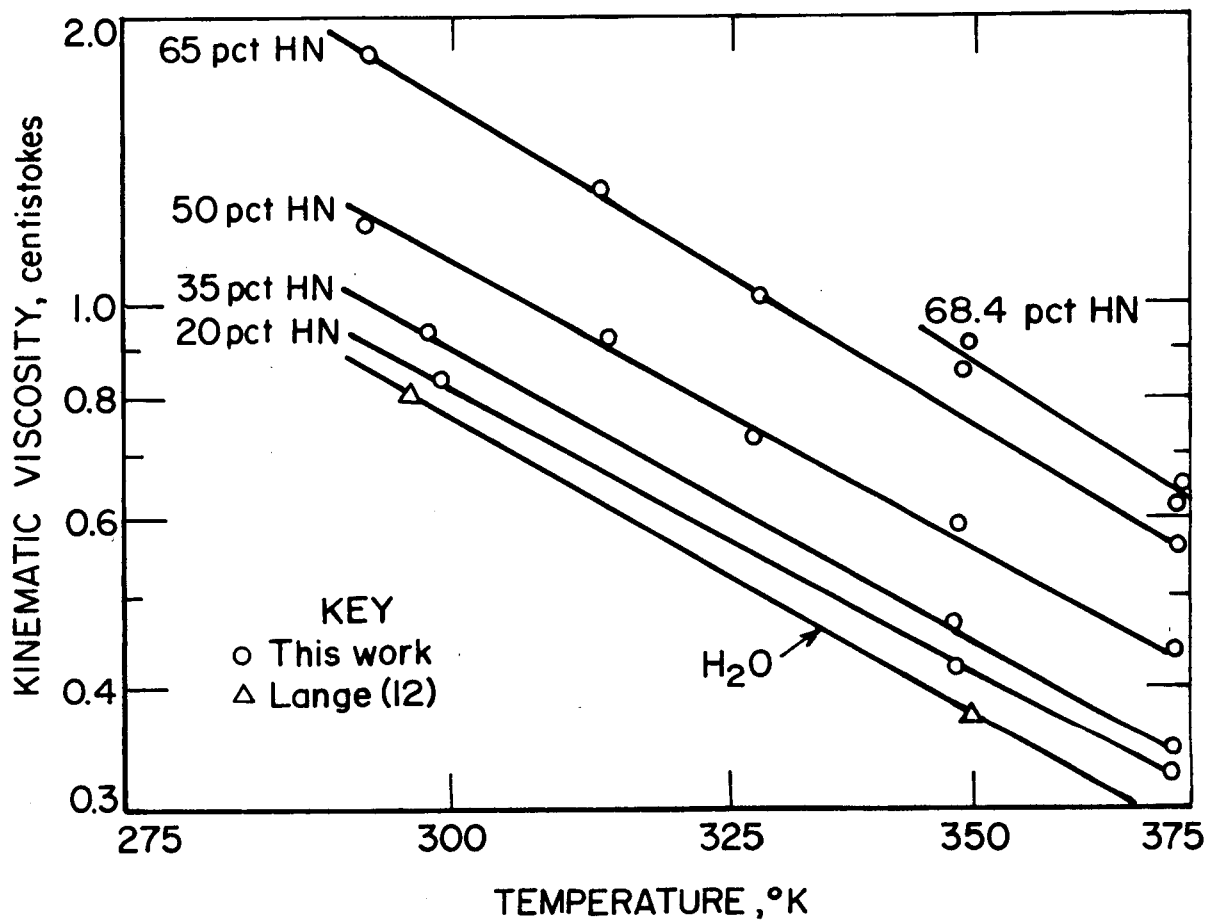


FIGURE 9. - Kinematic Viscosity of HN/Hydrazine Solutions at Various HN Concentrations as a Function of Temperature.



PX3-103
719

FIGURE 10. - Kinematic Viscosity of HN/Water Solutions at Various HN Concentrations as a Function of Temperature.

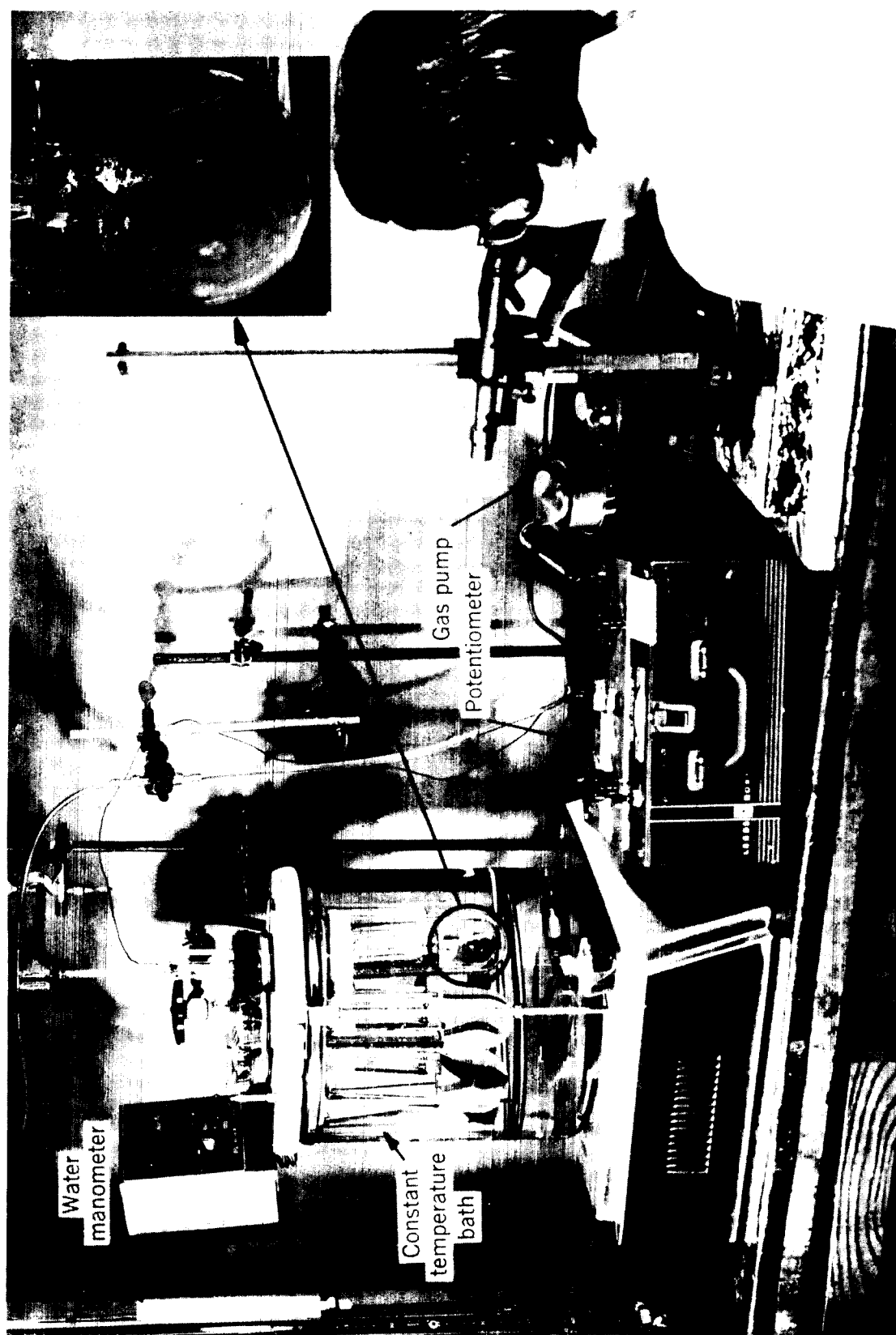
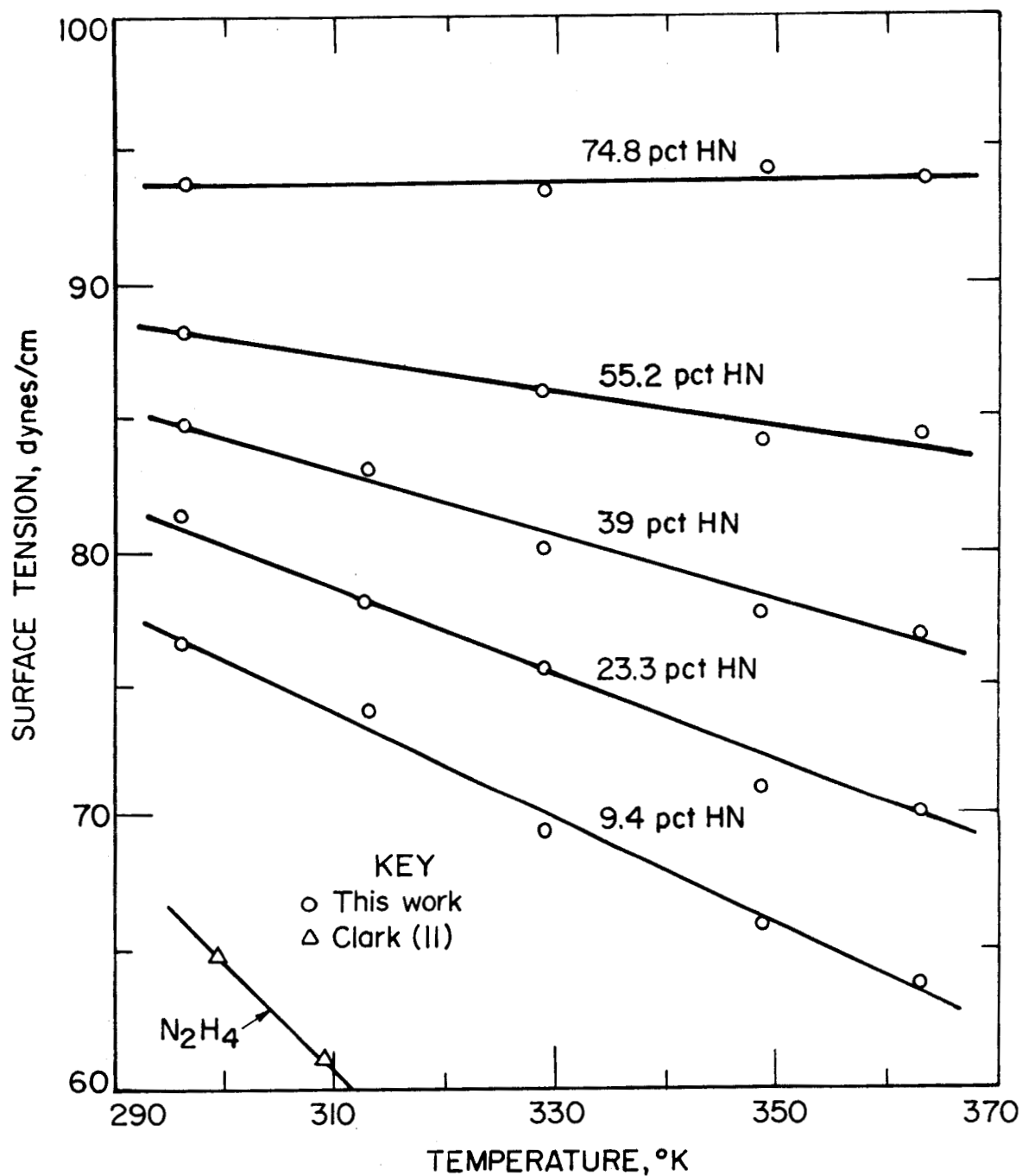
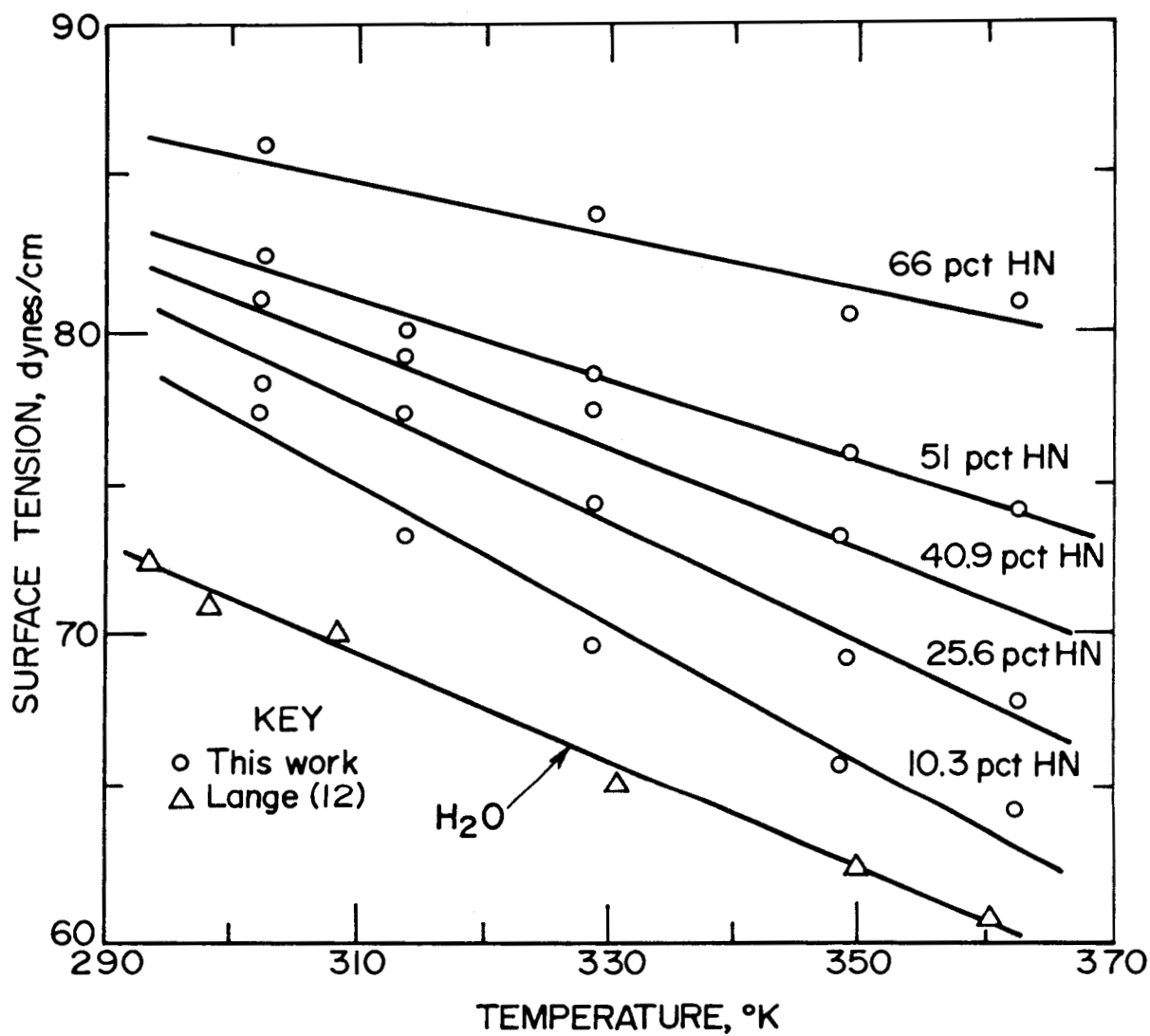


FIGURE 11. - Experimental Apparatus Used in the Measurement of the Surface Tension of $\text{HN}/\text{N}_2\text{H}_4$ and $\text{HN}/\text{H}_2\text{O}$ Solutions.



Px3-103
718

FIGURE 12. - Surface Tension of HN/Hydrazine Solutions at Various HN Concentrations as a Function of Temperature.



PX3-103
717

FIGURE 13. - Surface Tension of HN/Water Solutions at Various HN Concentrations as a Function of Temperature.

Vapor Pressure, Heat of Solution, and Liquidus Isotherms of HN/N₂H₄/H₂O Solutions

The vapor pressures of two HN/hydrazine mixtures were determined by Vango and Krasinsky (10). Results are given in figure 14. Also shown, for comparison, are the vapor pressures of water and of hydrazine in the same temperature range. The heat of solution of HN in water/hydrazine systems for different compositions of the three components measured by Elverum and Cole (14) is shown in figure 15, while figure 16 gives the liquidus isotherms for the ternary system HN/hydrazine/water. The last figure is from a report by Corcoran and coworkers (15).

Explosion Characteristics of HN and Its Solutions

Since it has been established that HN constitutes a major portion of the solids in engine residue when the fuel was either N₂H₄ or Aerozine-50 (A-50) [a 50:50 mixture by weight of N₂H₄ and unsymmetrical dimethylhydrazine (UDMH)], it was deemed necessary to completely investigate and understand its explosive characteristics. The Bureau studied the explosive characteristics of solutions of HN and of crystalline and cast HN. For a detailed view of HN as an explosive, a review of the available literature, in conjunction with Bureau results, is presented in this section. There are numerous methods by which explosive materials are evaluated, with regard to their explosive potential, and compared. Some of the methods are simple, and even crude, while others are sophisticated. These methods include, among others, autoignition, ignition by external initiators, impact sensitivity, and detonation.

Each of the methods has its merits and drawbacks; the methods are not reviewed here, only the results are given. Of necessity then, there may appear to be a lack of connection between the various sections.

Thermal Stability of HN

The thermal stability of HN under atmospheric conditions has been studied by numerous investigators, and there seems to be general agreement regarding the fact that the pure material decomposes explosively at about 300° C. Rosen (16) measured the ignition temperature of HN using the "Bruceton up-and-down" method (17), which gave a reproducible 50-pct probability of ignition at 307° C.

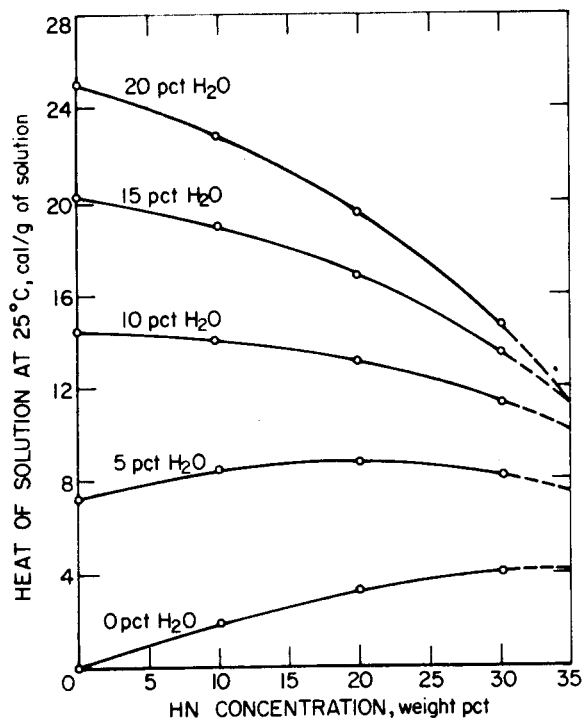


FIGURE 15. - Heats of Solution of HN in Water/Hydrazine Systems.

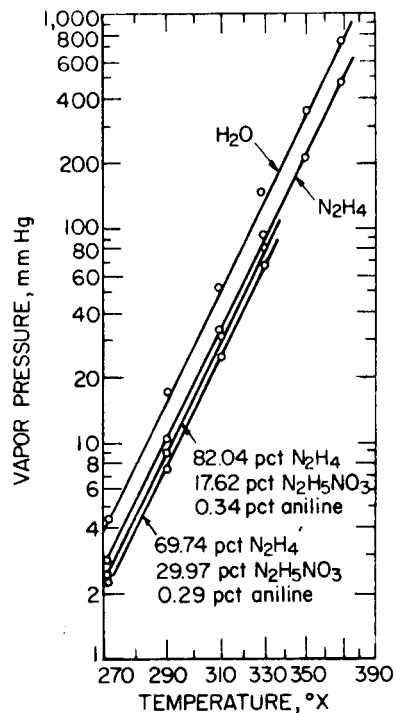


FIGURE 14. - Vapor Pressure for Water, Hydrazine, and Two HN/Hydrazine Solutions.

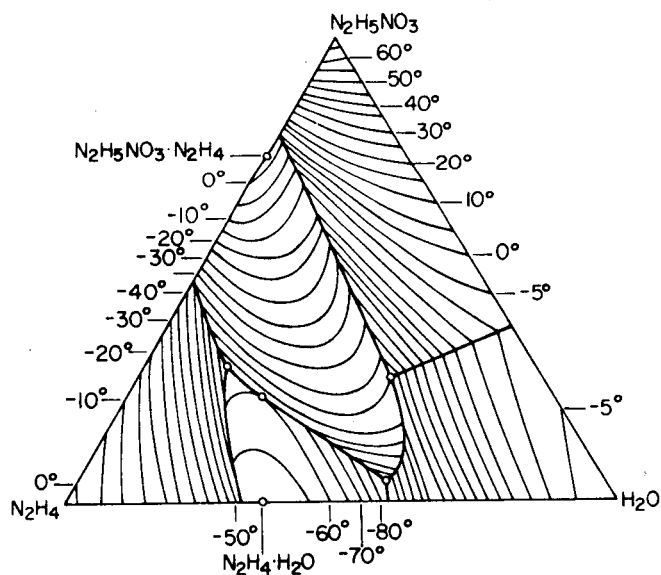


FIGURE 16. - Isotherms of the System HN/N₂H₄/H₂O.

Bureau experiments with molten HN for studying the initiation of detonations in unconfined thin films ([0.25 cm thick] by means of electrically heated Nichrome⁴ wire and by open flame), indicate that the films support combustion when ignited but do not detonate. Furthermore, the flame extinguished upon removal of the ignition source. These results agree with those of Shidlovskii and coworkers (18); they were not able to initiate detonation of HN, contained in glass tubes of small diameters, using electrically heated wire. To achieve stable burning, they found that the addition of about 10 weight percent of potassium dichromate to the HN was necessary. Levy and coworkers (19) found that a tamped strand of HN, containing 2 pct by weight of magnesium oxide burned in air at 1 atm, but a similar strand of pure HN did not burn. These experiments indicate the need for a strong oxidizer, albeit in small quantities, for stable combustion.

Detonation Velocity of HN

The residues found in the attitude control engines coat the inside walls of the engines as thin films. Thin films can be initiated to detonate at either high or low velocities. The velocity of detonation is one indicator of the destructive force of the detonation.

The velocity of detonation of explosives can be measured by various techniques including thin films. Results obtained by these techniques are then compared and, in general, should agree. A review of the literature revealed that the detonation velocity of HN was determined by a few researchers.

Price and coworkers (20) found a detonation velocity of 8,510 m/sec for HN at a density of 1.59 grams/cm³ for a 6.3-cm-diam charge of pressed HN. Medard (6), using a 3-cm-diam by 170-cm-long, pressed HN charge, found that the maximum detonation velocity occurred at a density of 1.3 grams/cm³. Moreover, Clairmont, Jaffe and Price (21) established that such maxima are likely to occur for explosives for which the critical diameters⁵ increase with density. In fact, the detonation velocity is not uniquely defined by density and diameter; the same velocity can be exhibited at two density values. Also of interest is the fact that as the critical density is just exceeded for each diameter, the shock-induced reaction fails but nevertheless persists and propagates as far as three or more diameters. The results of these investigations are shown in figure 17. From these results it was concluded that HN does belong to this group of explosives for which the critical diameter increases with increasing packing density.

The detonation velocity of thin films of molten HN at 75° C was measured at the Bureau to be 8,500 m/sec.

⁴Reference to specific brands, equipment, or trade names in this report is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

⁵The critical diameter is the minimum charge diameter at which propagation of a stable detonation is possible.

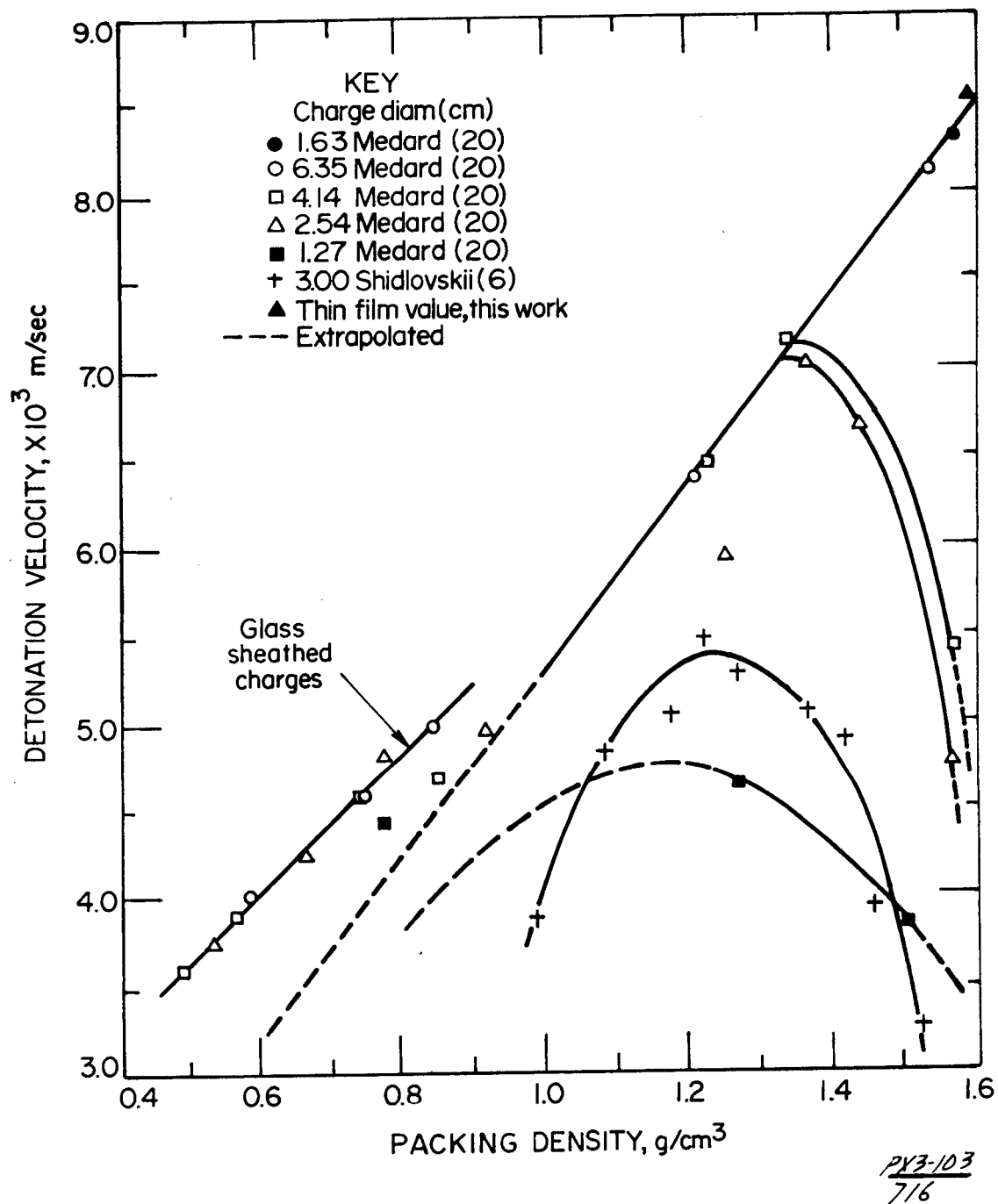


FIGURE 17. - Detonation Velocity of Pressed HN as a Function of Density for Various Charge Diameters.

Impact Sensitivity of HN

Impact sensitivity tests conducted at the Bureau, using the "Bruceton up-and-down" method (17), gave values--for 50-pct probability for ignition--of 175 Kg-cm for the cup and plunger test and 50 Kg-cm for the ERL type 12 tool test (22).⁶ In similar experiments, Smith and Walton (23) reported a value of 32 Kg-cm for a 50-pct probability of ignition for the ERL type 12 tool. Medard (6) obtained values of 200 to 250 Kg-cm, by dropping a 1 Kg weight from heights of 2 to 2.5 meters. The latter height gave 50-pct probability. Seamans and Dawson (24), using a carefully designed cup and puncture of a retaining steel diaphragm as evidence of combustion and hence as a sign of a positive test, have obtained a 50-pct value of 20.3 Kg-cm.

The impact sensitivity values quoted here do not agree at all and vary from 20 to 250 Kg-cm. The purity of the HN used in the tests is of extreme importance. Small traces of water, nitric acid, and/or other impurities affect the results. The packing density of the sample is also influential. Therefore, these results are not to be compared or evaluated in a critical manner.

Fast Chemical Reactions of HN

Even if the residues accumulating in the engine are not explosives, it is possible that they may react explosively with either propellant (fuel or oxidant) when the latter are injected into the engine combustion chamber; this possibility was evaluated.

Studies of the reaction of HN with various hypergolic propellants, by the Bureau, showed that crystalline HN and liquid NTO react vigorously on contact. Moreover, a DSC study of a frozen mixture containing equal proportions by volume of HN and NTO, initially at -100° C, showed that such mixtures react exothermically when the temperature reaches -60° C. This is a significantly lower temperature than the melting point of NTO (-11.2° C), and indicates a reaction between the two solids.

Additional experiments were conducted to determine if the fast reaction between HN and NTO is capable of initiating a detonation in the HN. In this study, liquid NTO was forcibly injected under the surface of 200 cm³ of molten HN contained in glass vessels; similar experiments were performed with HN/hydrazine and HN/A-50 solutions. Although considerable reaction was evident, none of the reactions approached an explosion.

Extensive materials compatibility studies have been conducted with HN by many investigators. Medard (6) found that weakly nitrated explosives could be appreciably sensitized by a small amount of HN. This fact is of importance when the fuel used is either UDMH or A-50. In the infrared and

⁶These are standard tests for measuring the impact sensitivity of explosives and are described in related literature.

mass spectroscopy studies of the products of reactions in the Bureau's 2-D engine and gas flow reactor, there was evidence to indicate the presence, in small quantities, of nitrated compounds, which were not further identified. They may be sensitized by the HN present and become potential hazards. Hodgkinson (25) reported that detonation occurred 40 pct of the time if small cobalt cubes were dropped into molten HN, and 20 pct of the time if nickel chips were used. Similar experiments done by the Bureau with heated molybdenum chips and molten HN showed no evidence of a reaction. Hodgkinson attributed the reaction to the formation of a small amount of metal azide, formed on the metal cubes, which explosively decomposes and detonates the remaining HN.

Explosion Characteristics of Systems Containing HN

Thin Film Detonation Velocity

Detonation velocity and critical film thickness were determined by measuring the velocity of a detonation as it traveled through a wedge of the solution and by observing the film thickness at which the detonation was extinguished. A complete description of the experimental apparatus, as well as of the technique and testing procedures, is given in a report by Ribovich (26). Presented here (fig. 18) is only a photograph of the apparatus for ease of understanding. The results of these experiments showed the occurrence of both a high and a low velocity detonation. The high velocity detonation (7,600 to 8,500 m/sec) started near the initiating explosive, in the thick portion of the film, and converted to a low velocity detonation (1,400 to 2,400 m/sec) when the film reached a critical thickness for the high velocity detonation. Table 4 summarizes these results. The theoretical Chapman-Jouguet shock velocities of HN/N₂H₄ mixtures were computed with the TIGER computer program (27); these results are given in table 5. Results of the computed values are in good agreement with the experimental values of the high velocity detonation. Figure 19 shows a representative pressure trace obtained in these experiments.

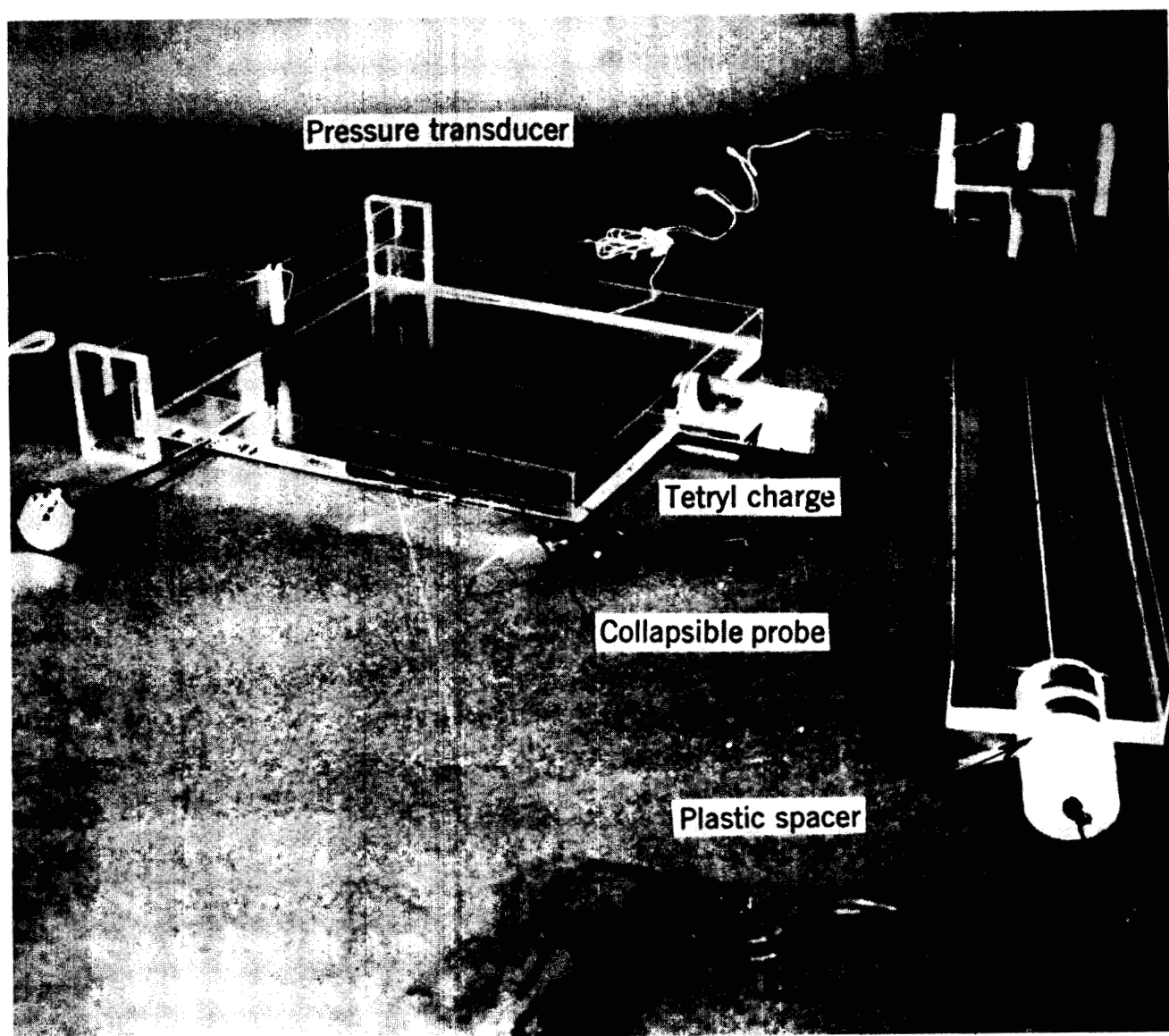


FIGURE 18. - Thin-Film Detonation Apparatus.

TABLE 4. - Detonation velocities and critical film thicknesses (CFT)
of both low- and high-velocity detonations of molten HN,
HN-water, and HN-hydrazine solutions at 75° C

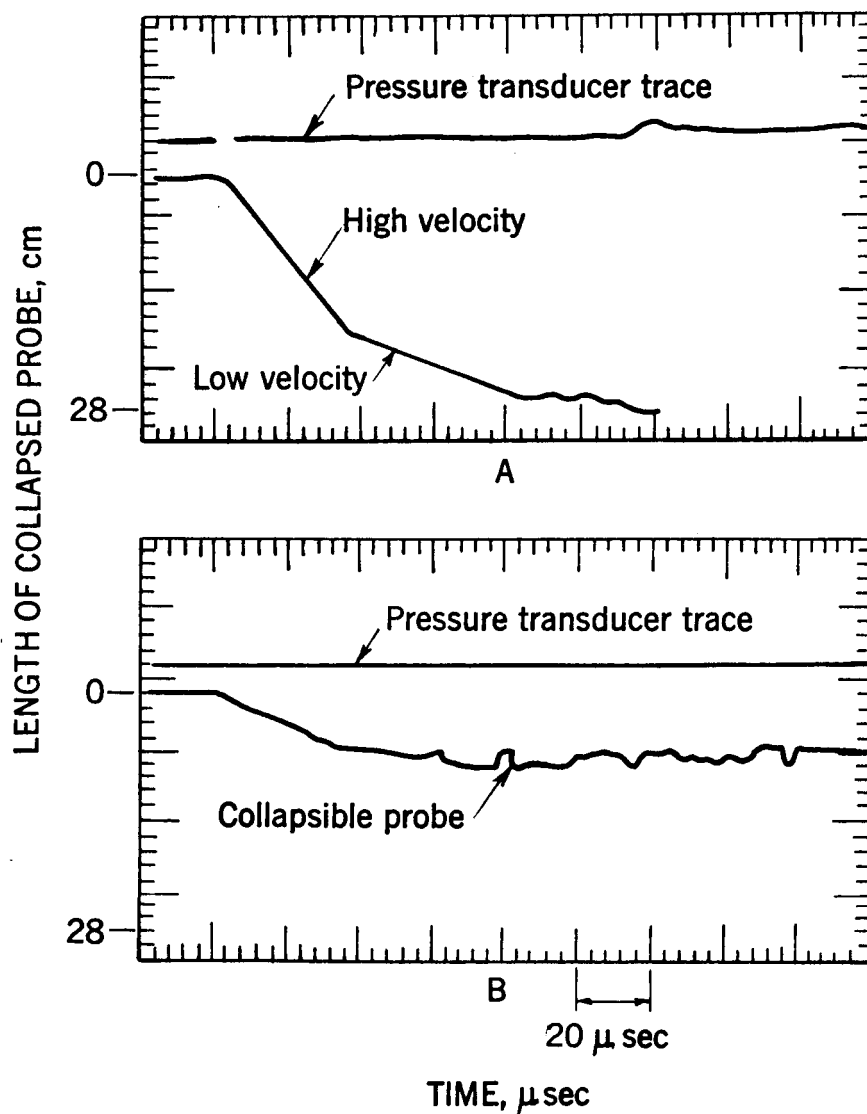
Composition	Liquid HN concentration, weight-percent	Detonation velocity			
		High		Low	
		Velocity, m/sec	CFT, cm	Velocity, m/sec	CFT, cm
HN.....	100	8,500	0.127	1,400	¹ ≤0.025
HN/water...	85	7,600	.305	2,400	≤.025
	75	Not observed		2,100	.330
	65	No propagation			
HN/N ₂ H ₄	80	8,600	.076	1,800	≤.025
	60	8,200	.076	Not observed	
	40	7,800	.254	2,200	.076
	20	No propagation			

¹0.025 cm represents the limit of resolution of the apparatus.

TABLE 5. - Calculated constant volume explosion characteristics
of condensed phase HN/N₂H₄ mixtures
(initial pressure: 1 atm)¹

HN concentration, weight-percent	Final pressure, atm (x10 ⁵)	Final temperature, °K	Chapman-Jouguet shock velocity, m/sec
0	1.61	1,075	8,207
10	1.76	1,174	8,352
20	1.90	1,283	8,475
30	2.04	1,405	8,576
40	2.19	1,540	8,669
50	2.35	1,685	8,763
60	2.53	1,847	8,852
75	2.86	2.102	9,040
100	1.33	3,137	6,871

¹TIGER code computer program (27).



PX3-103
541

FIGURE 19 - Typical Oscillograms of the Pressure Transducer and Collapsible Probe Signals for: (a) Propagation of a Stable Detonation, and (b) No Propagation.

The range of detonable composition of the ternary system, HN/hydrazine/water, measured by Dwiggins and Larrick (28) is presented in figure 20. Their test-container consisted of a 7.5-cm-long by 2.5-cm-diam brass pipe, sealed at one end with a copper foil. A 50-gram tetryl pellet was used to initiate detonation. It is surprising, though, that brass and copper were used in the test equipment since N_2H_4 is known to be affected by copper. Small traces of copper ions exert a strong catalytic effect upon the oxidation of hydrazine by copper. Copper metal also increases the reaction rate of hydrazine with oxygen when present even in low concentrations of 0.5 ppm (29).

Since N_2H_4 is a strongly basic solvent and a good proton acceptor, it is to be expected that compounds containing active hydrogen will act as acids therein and be converted into corresponding hydrazine salts. Solutions of hydrazine sulfate in anhydrous N_2H_4 dissolve such metals as copper and aluminum (30). It is very likely that solutions of HN in N_2H_4 will act similarly with copper. Dwiggins and Larrick (28) have studied the compatibility of their test solutions with such materials as polyethylene, polystyrene, teflon, nylon, tantalum, titanium, and aluminum, but not with copper. The detonable thin-film binary HN solutions measured by the Bureau agree with the detonable region of the ternary triangle of figure 20. Dwiggins and Larrick (28) showed that HN/ N_2H_4 solutions containing less than 25 pct by weight HN, HN/water solutions containing less than 70 pct by weight HN, and ternary HN/ N_2H_4 /water solutions containing more than 55 pct by weight of water were not detonable under their experimental conditions. Subsequent Bureau studies showed that the boundary of the detonable region depended strongly on the size of the initiating explosive.

Although the residues found in the engines contained very small amounts of HN in a water solution, HN is highly deliquescent, and may have accumulated large amounts of water both before sampling and between sampling and analysis. Also, the residue, in a period of many pulses, may become more concentrated with salts and other reaction products.

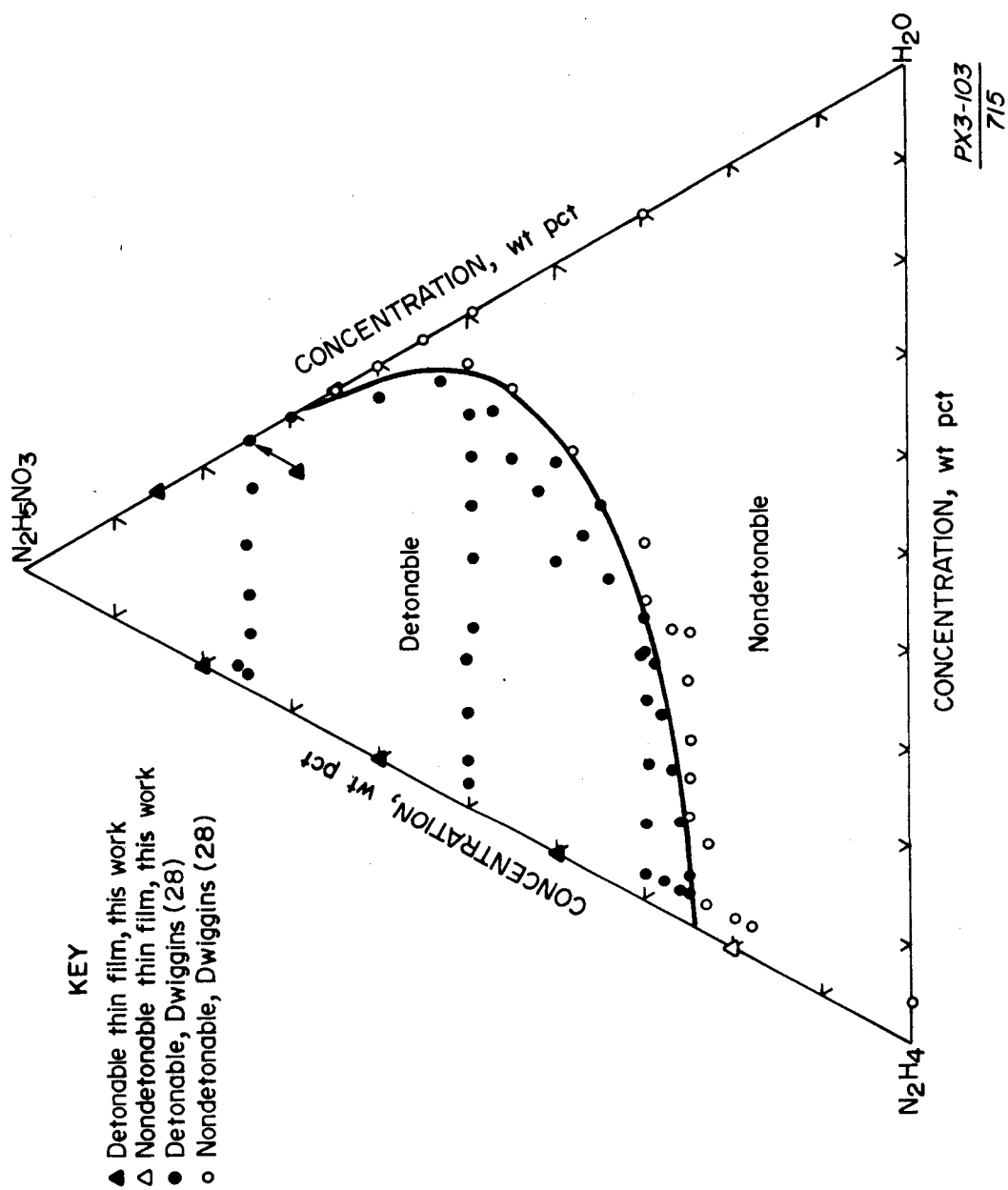


FIGURE 20. - Detonable Compositions of the Ternary System
 $\text{HN/Hydrazine/Water}$.

Detonation of Thin-Layer Wall Deposits of HN and HN Solutions
Via Gas-Phase Detonation

Detonation Initiation by Ethylene/Oxygen Detonation

It has been established that engine residues contain HN; it has also been shown that HN solutions of certain concentrations will support detonation, when suitably initiated. Although these concentrations are usually higher than the concentrations of HN normally found in engine residues, it is believed that the lower concentrations found in engine residues result by water adsorption on exposure to air. Based on these observations, it was also assumed that the engine residues not exposed to the atmosphere contain higher concentrations of HN, and if initiated, will support detonation. Sources of initiations were considered and investigated. One of the considered mechanisms concerned the possibility that a gas or heterogeneous phase detonation in the engine interior might initiate detonation of the wall deposits. The heterogeneous propellant mixture found in the engine has been studied in great detail by many investigators and need not be discussed here. The bibliography (volume I) contains many references on this subject. This heterogeneous mixture of liquid propellant drops within the propellant vapor can be hypergolic under the proper conditions. In the actual engine, if a heterogeneous detonation were to occur and, in turn, were to initiate the detonation of wall films, these two processes could not be differentiated from the resulting damage.

To determine the feasibility of this particular mechanism, we conducted a number of experiments in which HN was subjected to a gas-phase detonation of a stoichiometric C_2H_4/O_2 mixture. As is shown in subsequent sections of this report, this gas detonation alone does not destroy or otherwise damage the engine under the conditions cited.

In these experiments, the granular or molten HN sample was placed in the bottom of the test vessel (fig. 21), a detonable gas mixture (ethylene 25 pct, oxygen 75 pct) was added, and detonation was initiated in the gas mixture with an exploding wire. The motion of the detonation through the gas and the reaction front through the HN was measured with a continuous wire probe (31). The pressure developed at the interface between the HN charge and the gas mixture was measured with a resistive pressure transducer (32). Temporal correlation of the pressure and detonation position was provided by simultaneously displaying the two records on a single beam oscilloscope with a dual channel plug-in unit having a 1 Mc chopping rate. Associated instrumentation and related circuitry are shown in figure 22.

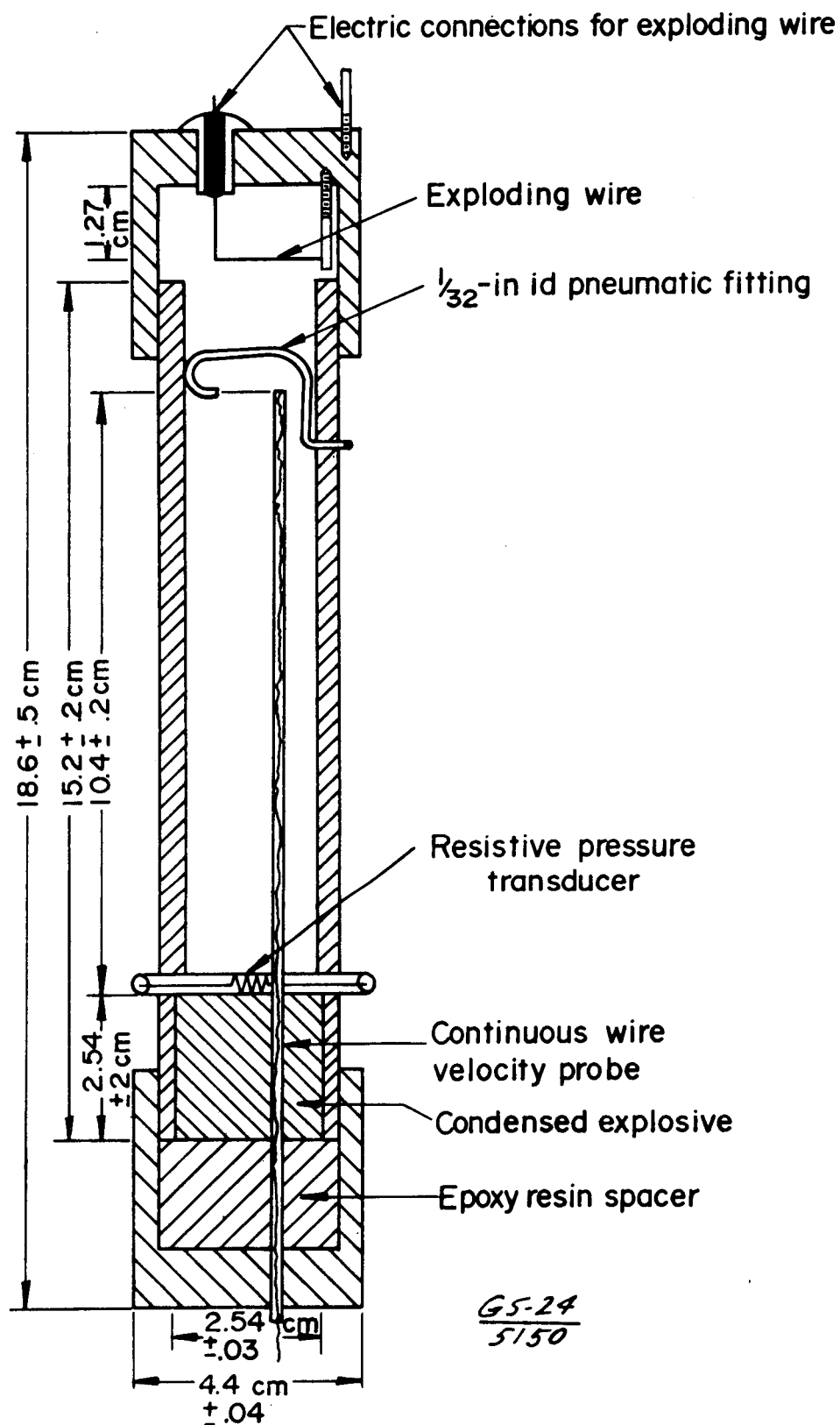


FIGURE 21. - Test Vessel for Studying Initiation of Detonation in Condensed Explosives by Gas-Phase Detonation.

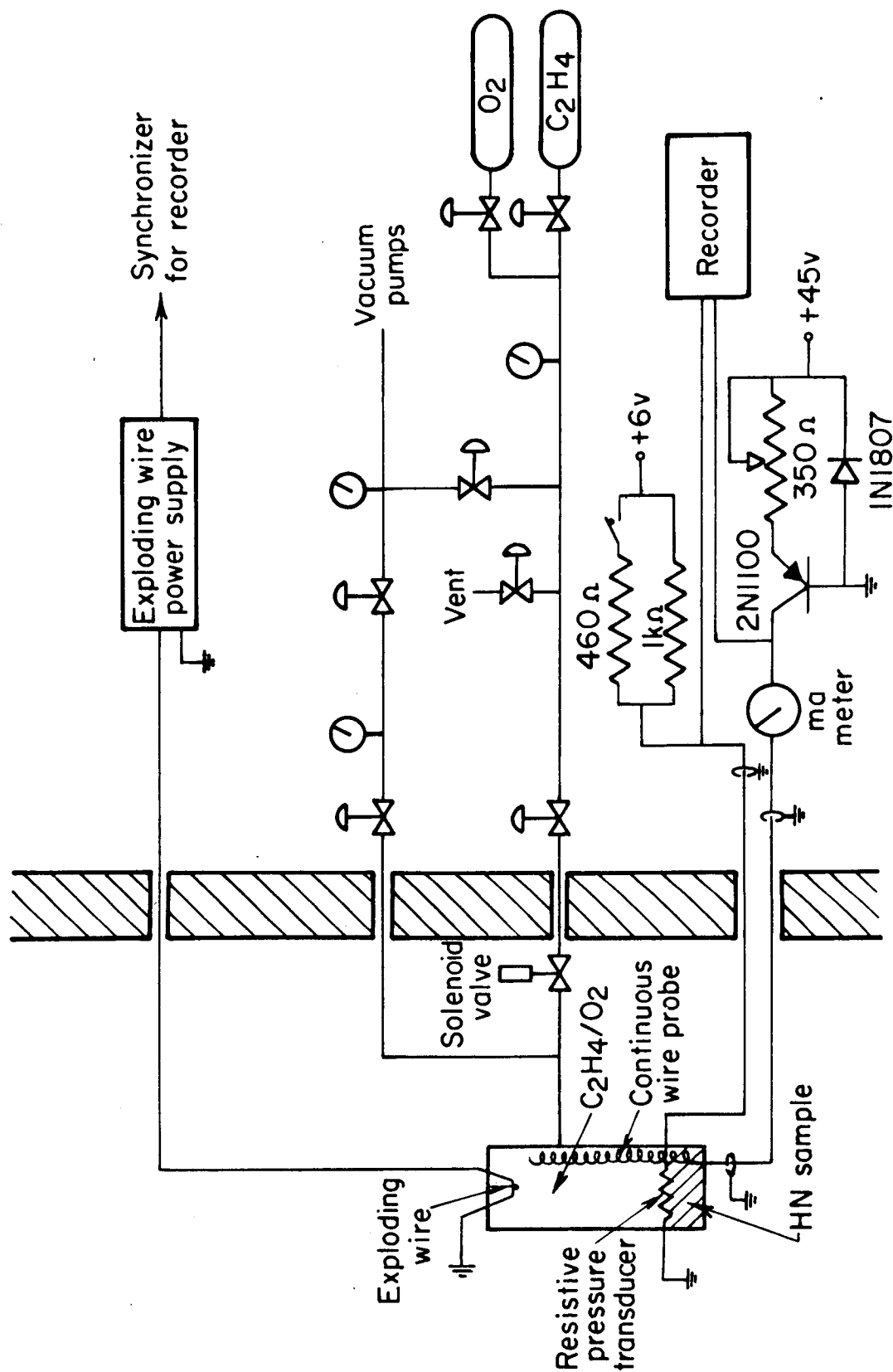
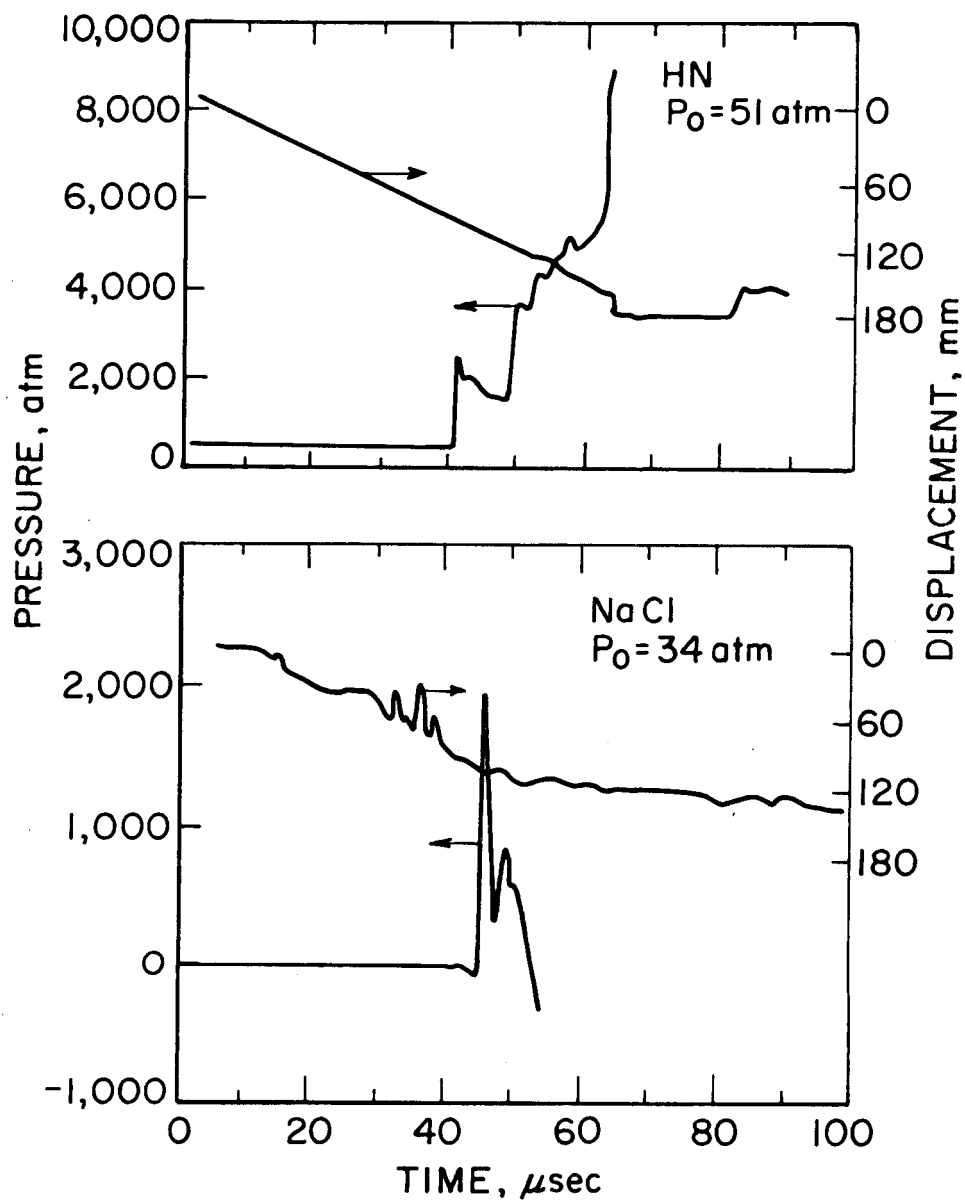


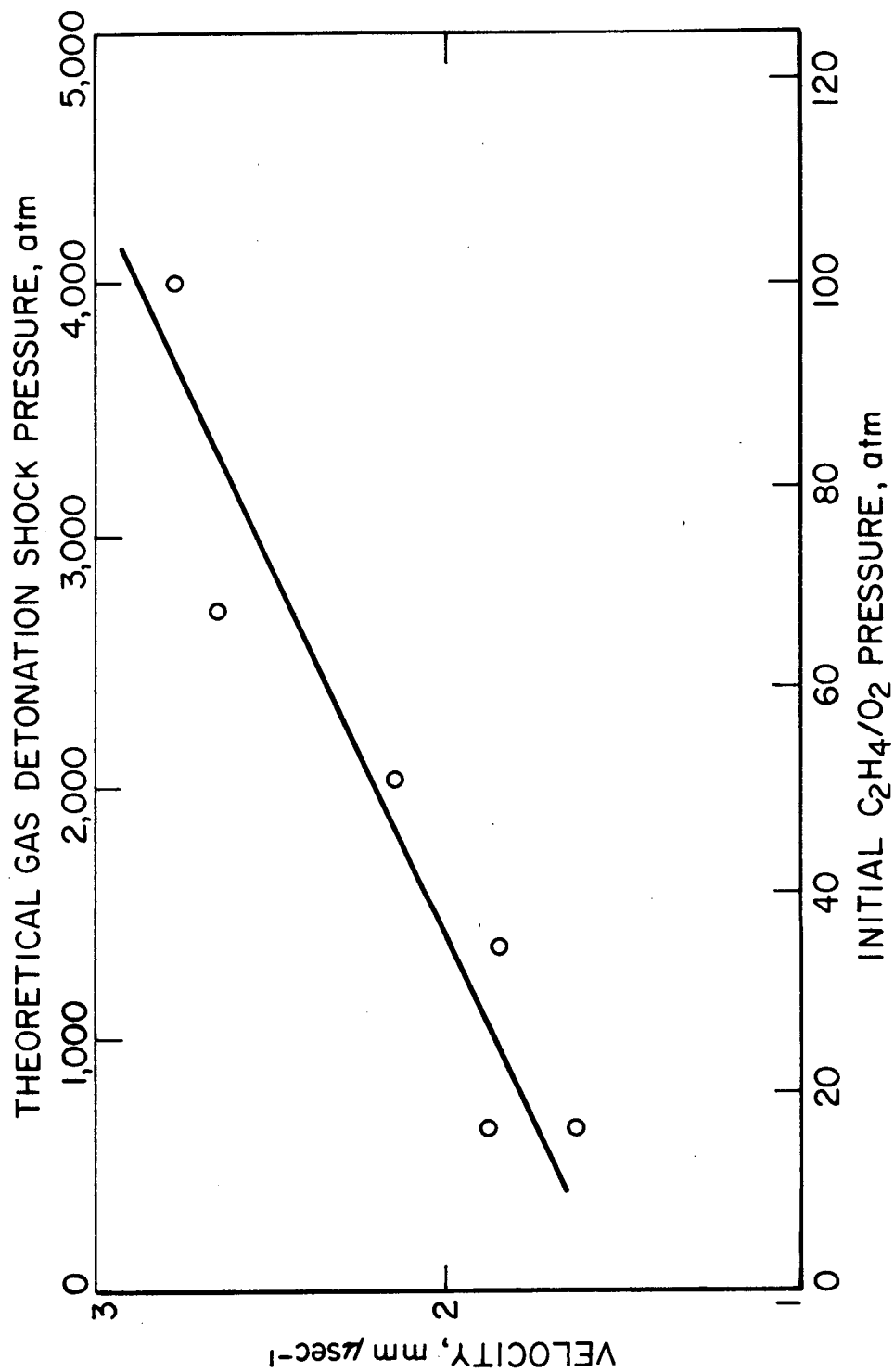
FIGURE 22. - Apparatus Used to Study Gas Detonation Initiation of Condensed Explosives.

The experiments were conducted with both granular and cast HN having densities of 0.7 and 1.6 grams/cm³, respectively. By varying the initial pressure of the gas mixture from 16.3 to 100 atm, it was possible to obtain incident shock pressures at the surface of the HN sample ranging from 475 to 4,300 atm. Reaction in the HN sample was evidenced by: (1) A large increase in the pressure at the surface of the HN charge following shock reflection, and (2) the propagation of a fast high pressure reaction front through the sample, as recorded by the continuous wire probe. Figure 23 shows typical pressure and displacement records obtained for granular HN and NaCl (a nonreactive material) samples. The pressure recorded for the HN sample is typical of reactive (explosive) materials. It shows the arrival of the incident gas detonation shock of 2,380 atm at the surface of the HN sample at 40 μ sec following explosion of the wire. This is the time it takes the gas detonation to travel from the exploding wire to the HN surface. This shock is followed by a slight pressure decay and then an abrupt pressure rise at 50 μ sec to a value in excess of 6,800 atm as a result of an exothermic chemical reaction in the HN. The record for the NaCl sample, with the same crystal size and bulk density as the HN sample, shows about the same incident shock (1,900 atm) followed by a rapid decay with no subsequent recovery and, therefore, no chemical reaction. The reaction front displacement records for the HN sample show a continuous transition from the gas detonation traveling at 2.2 mm/ μ sec to the HN sample traveling at about the same initial velocity. On the other hand, the NaCl displacement record shows the transmission of a decaying front velocity in the NaCl corresponding to an attenuated shock wave. Figure 24 shows a plot of the initial reaction front velocity in granular HN as a function of the initial ethylene/oxygen mixture pressure and as a function of the theoretical gas detonation shock pressure. Although not evident from figure 23, the displacement traces in the HN sample usually show a slight reaction front acceleration. Because of the limited sample length of 2.5 cm, this velocity does not reach the maximum value; but it is assumed that this front will accelerate until the velocity reaches the stable Chapman-Jouguet value of about 3.5 mm/ μ sec (33). The ratio of the maximum explosion pressure to the incident shock pressure varies from 2.8 to 1.3 at the lowest C₂H₄/O₂ initial pressure of 16 atm.



P64-73
385

FIGURE 23. - Surface Pressure and Continuous Probe Records for Granular HN and NaCl Samples.



PGH-73
386

FIGURE 24. - Initial Reaction Front Velocity in Granular HN as a Function of Initial Gas Mixture (25 pct C₂H₄/75 pct O₂) Pressure and Theoretical Gas Detonation Shock Pressure.

Damage to reaction vessels is also used as a semiquantitative measure of explosive strength. Figure 25 shows vessel fragments from HN and NaCl runs. The results shown in table 6 for granular HN and the extent of damage to the vessel depicted in figure 25, both indicate that the HN undergoes an explosive reaction when subjected to shock pressures equal to or greater than 520 atm (the lowest incident shock pressure investigated in these trials), and that the rate of the reaction front and the maximum pressure developed at the HN surface, as a result of chemical reaction in the HN, decreases with decreasing shock pressure.

TABLE 6. - Reaction pressures and propagation velocities in granular HN initiated by an C_2H_4/O_2 gas detonation

Initial pressure, atm	Gas mixture		HN reaction		
	Detonation shock pressure, atm ¹	Pressure ratio ¹	Maximum pressure, atm	Velocity, mm/μsec	Max. explosion pressure to incident shock pressure ratio
100	4,350 (3,950)	44 (39.3)	12,240	2.7	2.8
68	3,130 (2,650)	46	8,160	2.6	2.6
51	2,380 (1,970)	47	5,510	2.1	2.3
34	1,430 (1,290)	42	2,710	1.8	1.9
16	420 (600)	26	540	1.6	1.3
16	520 (600)	32	680	1.9	1.3
10	-	- (36.4)			
1	-	- (33.5)			
NaCl Reaction					
100	5,240 (3,950)	52	Nonreactive decaying		

¹Quantities in parentheses are theoretical Chapman-Jouguet detonation pressures for the stoichiometric C_2H_4/O_2 combinations that were used in the tests.

LEGEND

Figure	Sample	Initial gas pressure, atm
1	Granular HN	100
2	Cast HN	100
3	Cast HN	68
4	Cast HN	68
5	Granular NaCl	100

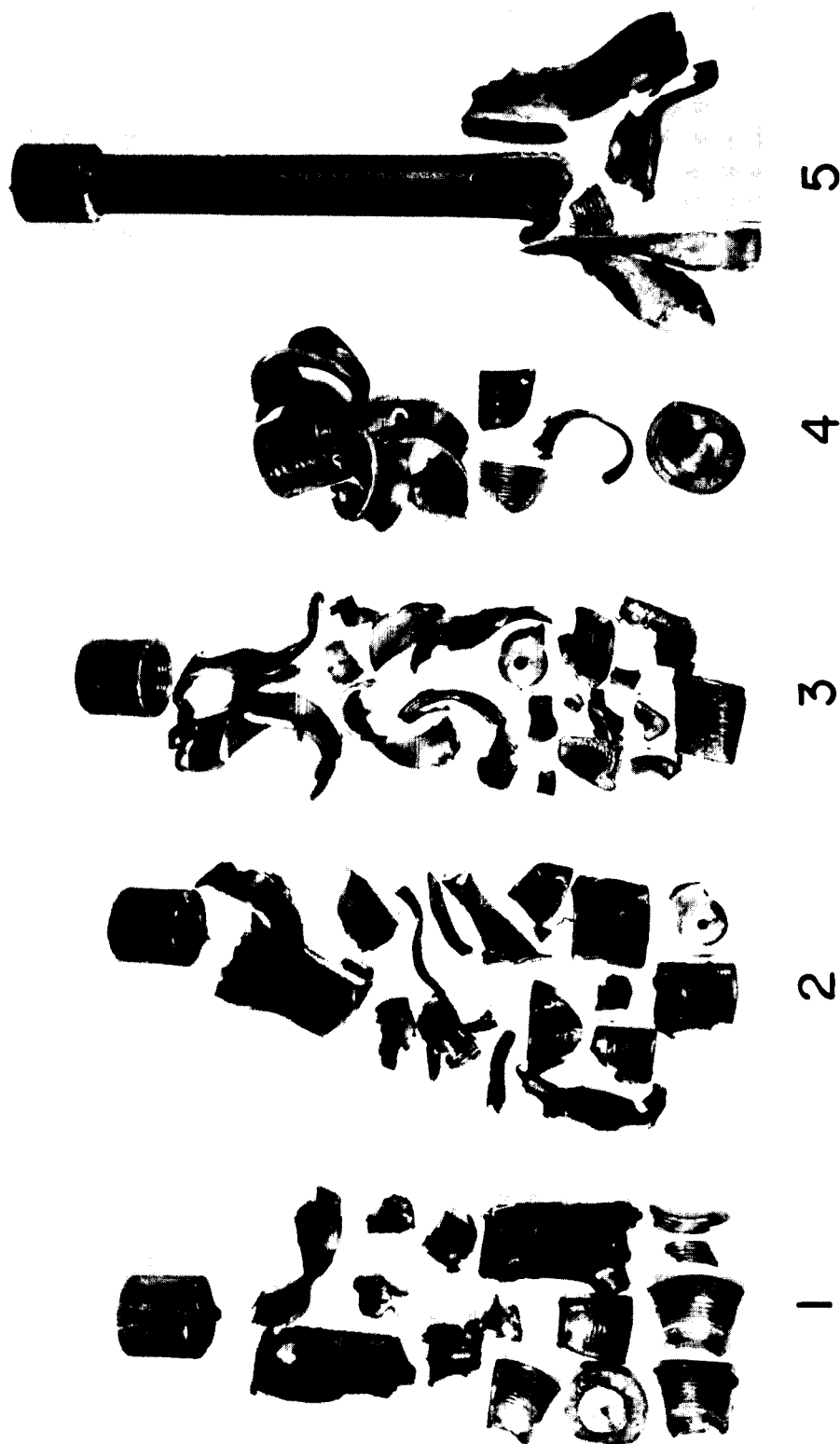
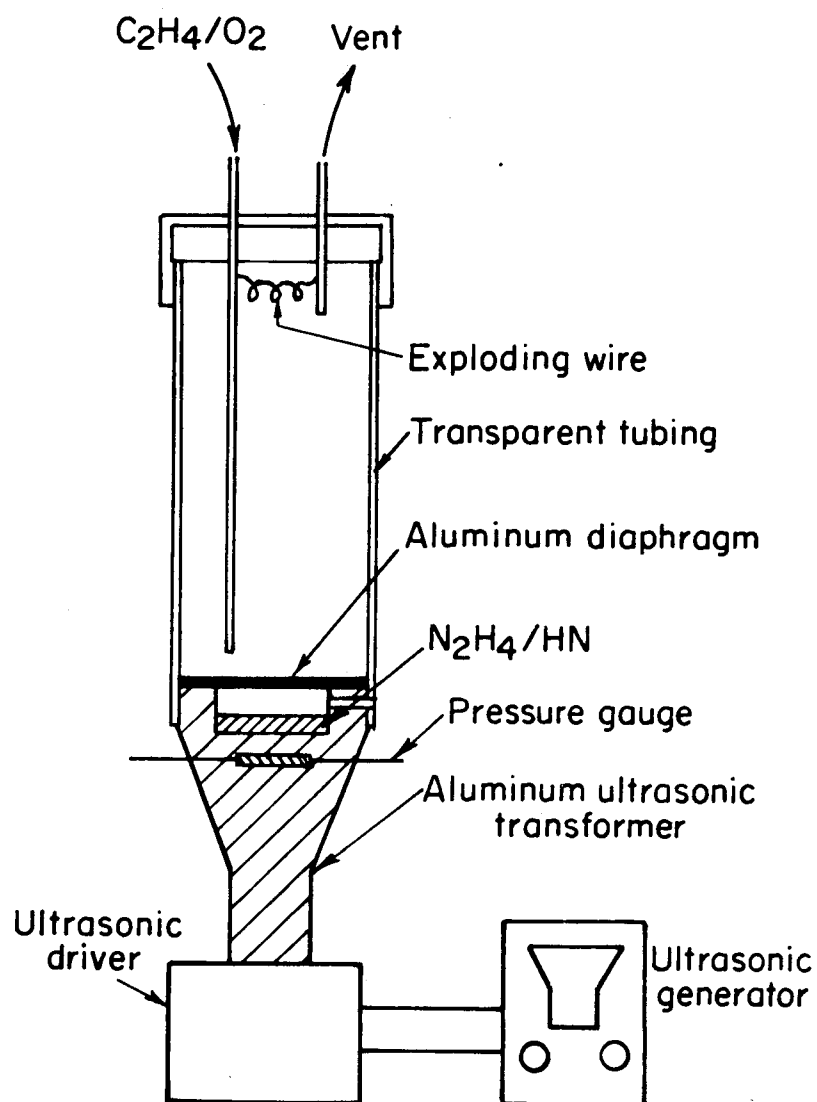


FIGURE 25. - Test Vessel Fragmentation Patterns Following Explosive (1-4) and Nonexplosive (5) Reactions.

These results show that a gas detonation can initiate an explosion in cast or granular HN deposits. The normal initial pressure of gaseous propellants in the engine at the time of engine ignition is of the order of 1 atm. In subsequent similar tests described in the following section of this volume, an initial gas pressure of 1 atm was used.

Shock Sensitivity of Cavitated HN Solutions

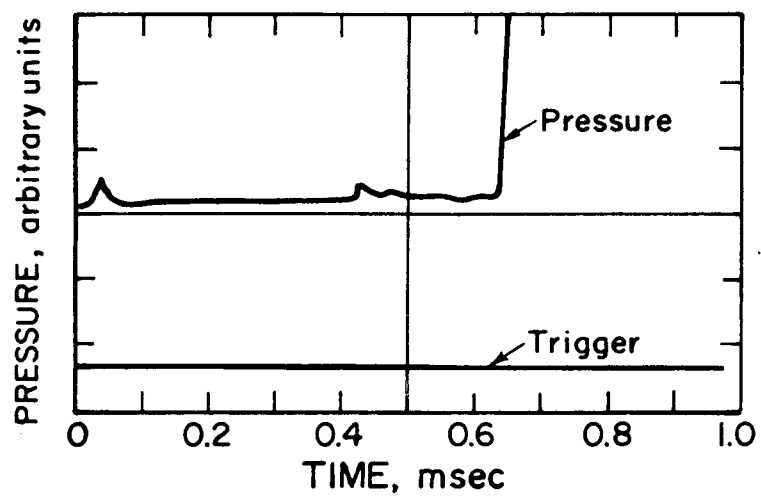
In addition to the possibility of a gas-phase detonation initiating an explosive reaction in thin films of HN, either crystalline or molten, it has also been suggested that the shock sensitivity of cavitated HN solutions is considerably higher than those of uncavitating systems. Photographs of plastic engines show considerable wall film cavitation during engine operation. This theory primarily originates from the fact that cavitation is believed to be responsible for the very low shock sensitivity of nitroglycerin (34) and of other condensed phase explosives. The apparatus used in this investigation is shown in figure 26. A gas-phase detonation propagating in a stoichiometric C_2H_4/O_2 mixture (25 pct C_2H_4 /75 pct O_2) impacts a cavitated HN/N_2H_4 solution. Cavities are formed in the liquid by two processes; by ultrasonic radiation which produced relatively small bubbles whose growth followed the same frequency as the applied radiation, and by lowering the gas pressure above the HN solution sufficiently to induce boiling. The latter procedure appeared to be more representative of the processes occurring in the rocket engine and, consequently, it was the technique used in the majority of these experiments.



P6H-73
387

FIGURE 26. - Apparatus to Study the Gas Shock Initiation of Detonation in Cavitating HN/N_2H_4 Solutions.

The HN solution was separated from the C_2H_4/O_2 mixture by a thin aluminum diaphragm (fig. 26). This prevented oxidation of the N_2H_4 in the solution and facilitated lowering the pressure over the sample without affecting the C_2H_4/O_2 initial mixture pressure of 1 atm. In order to monitor the response of the HN/ N_2H_4 sample to the gas-phase detonation shock, an explosion gage (32) embedded in the aluminum ultrasonic transformer and located immediately below the center of the sample was used to record the shock pressures transmitted through the sample. An oscilloscope recorded the response of the explosion gage. If the HN sample is not initiated to an explosive reaction, the apparatus is undamaged and the oscilloscope records a pressure pulse (shock) of small magnitude. However, when explosion does occur, the ultrasonic transducer is damaged beyond repair and the lower portion of the apparatus is completely destroyed and the oscilloscope trace goes off scale because the gage is destroyed. Experiments were performed with both cavitated and uncavitated solutions, and the results of these experiments showed that both the cavitated and uncavitated HN/ N_2H_4 solutions containing more than 75 pct by weight of HN exploded consistently when impacted with the C_2H_4/O_2 detonation. Figure 27 shows a typical explosion gage pressure record. The first pressure peak in this record, occurring at 0.42 msec, was shown to be the shock transmitted into the sample from the C_2H_4/O_2 detonation. The second rise in the pressure trace, which takes it off scale, is due to the explosive reaction of the HN/ N_2H_4 solution. That the first peak corresponds to the shock from the gas-phase detonation can be shown by a similar experiment with an inert material like water; this same peak occurs with the inert material. The time delay between the passage of the shock from the gas detonation and the off-scale pressure rise due to the explosive reaction of the HN/ N_2H_4 solution was unexpectedly large (~ 0.2 msec). It raised the question whether the shock from the gas detonation was responsible for the initiation of the explosion in the solution. This delay can be most readily explained if one assumes that the explosive reaction is initiated thermally by the presence of the hot C_2H_4/O_2 detonation products rather than by the gas detonation shock. The shock pressure ratio associated with a stoichiometric C_2H_4/O_2 detonation for an initial pressure of 1 atm is approximately 34 (table 6). This is approximately one-half the average detonation pressure ratio calculated for a N_2H_4/NTO mixture (table 7), which shows the calculated detonation pressure ratios for N_2H_4 mixtures of various ratios at an initial pressure of 1 atm. Calculations were based on the NASA-Lewis computer program for computation of Chapman-Jouguet detonations (35). The results of these experiments demonstrate that although the shock from a C_2H_4/O_2 detonation, initially at 1 atm, is apparently not sufficient to initiate detonation in HN/ N_2H_4 solutions containing as much as 75 pct HN, the hot products from such a gas-phase detonation could do so. From these results, we conclude that a thermal initiation of detonation of a HN/ N_2H_4 solution on the walls of the engine by a N_2H_4/NTO gas detonation is possible. However, the detonation pressure of the N_2H_4/NTO , being twice as large, may initiate detonation of a HN/ N_2H_4 solution on the engine walls.



P6H-73
388

FIGURE 27. - Pressure Record of Cavitation Experiment.

TABLE 7. - Calculated detonation pressure ratios for various
 N_2H_4 /NTO gas mixtures at an initial pressure
of 1 atm¹

Fuel	Oxidant	Volume percent, fuel	O/F mole ratio	Pi, atm	Pf, atm	Pi/Pf atm	Tf, °K	Detonation velocity, m/sec
C_2H_4	O_2	25	3	1	33.5	33.5	1,178	2,376
N_2H_4	N_2O_4	80	0.25	1	59.8	59.8	3,574	2,690
N_2H_4	N_2O_4	67.0	.5	1	61.5	61.5	3,760	2,497
N_2H_4	N_2O_4	57.0	.75	1	59.0	59.0	3,629	2,323
N_2H_4	N_2O_4	50.0	1	1	56.4	56.4	3,456	2,192

¹Based on the NASA-Lewis computer code (35).

Gas-Thin Film Detonation Transition Studies

One final series of Bureau experiments in this area was made to determine if a gas-phase detonation, moving through the RCS engine from injector face to throat, for example, could in any way consume in an explosive manner the combustible (though not necessarily detonable) residue deposited on the engine wall.

Loison (36) was the first to investigate the possibility of a detonation propagating down a pipe containing gaseous oxygen and coated with a thin film of combustible substance. Using a 91-meter long pipe approximately 0.8 cm in diameter, he was able to observe a stable detonation traveling at ~ 1,100 m/sec using lubricating oil for the thin film. Ragland, Dabora and Nicholls (37), in similar experiments, used diethylcyclohexane as the fuel film in an oxygen atmosphere; they measured detonation velocities ranging from 970 to 1,150 m/sec and pressure ratios ranging from 10.5 to 17, respectively. High speed photographic films of these latter studies showed that the chemical reaction originated at the wall and spread in toward the center. Both convex and concave reaction fronts were observed.

Bureau experiments, using the apparatus shown in figure 28, were performed to study the initiation of detonation in a tube coated on the inside with a HN/N_2H_4 solution and filled with various gases (air, oxygen, or nitrogen). To provide a uniform wall deposit of the desired solution, the tube was slowly rotated in a lathe during the course of the experiment. Furthermore, a 0.61-cm-diam aluminum rod, the length of the test section, was placed in the test section; it rolled on the bottom as the tube rotated and assisted in providing and assuring a uniform distribution of liquid on the wall.

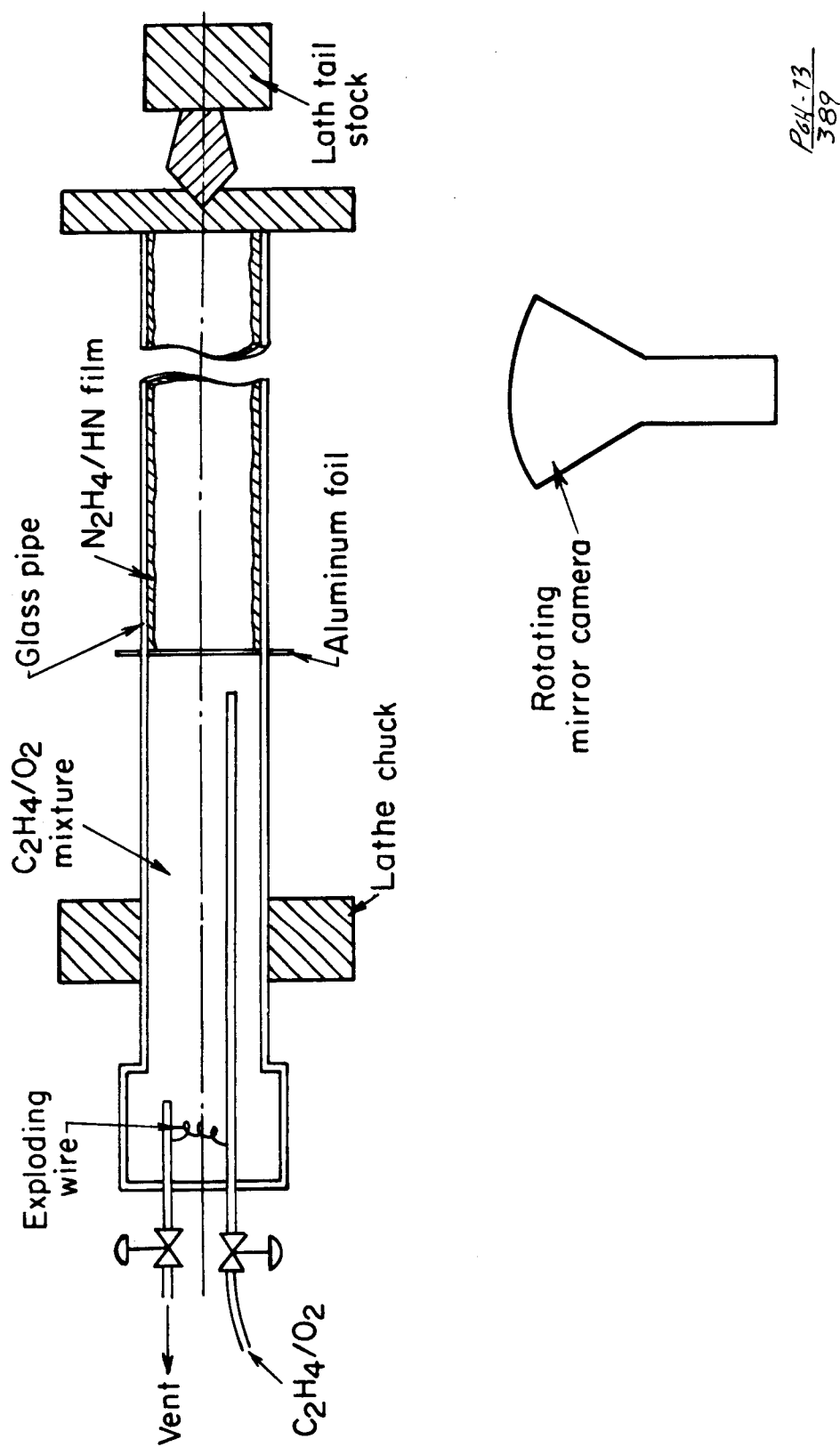


FIGURE 28. - Heterogeneous Detonation Apparatus

Although time did not permit developing methods for measuring the film thickness, it was estimated, from the total amount of liquid used in the tests, to be about 0.06 to 0.07 mm thick. A detonation initiated by an exploding wire in the left-hand compartment, using a stoichiometric C_2H_4/O_2 mixture at an initial pressure of 1 atm, transmitted a strong shock into the test section. Water, n-decane, N_2H_4 , and HN/N_2H_4 solutions were used at various times as the thin films. The test section containing the liquid film was flushed prior to firing with either nitrogen or oxygen in order to assess the effect of the environmental gas on the resultant combustion process. The progress of the shock through the test chamber was recorded by means of a streak camera. A typical streak record is shown in figure 29. Such records as these were used to determine the velocity of the shock front as a function of the distance of travel into the test chamber. The Mach number (the ratio of the velocity of the shock front to the sound velocity in the reactant mixture ahead of the front) was calculated for these tests and was used as the criterion for assessing the results. The results for various films at various atmospheres are shown in figures 30 to 34, inclusive.

Figure 30 which shows the propagation of a shock through the test chamber containing only air and no film, and illustrates the linear decay of the shock velocity as it propagates the length of the tube. The same type of results, this time with the test chamber containing a water film, are also depicted in figure 30 and we can see that the shock decays much more rapidly with the water film than when the walls are dry. This is to be expected since the water removed from the walls by the shock is vaporized in the hot gases following the shock and, in this manner, removes energy from the driving gases. No explanation is offered as to the upward bend of the water film curve at its termination. The results shown in figure 31, for n-decane were a little disappointing in that this material was expected to detonate consistently with this particular initiating device. However, only in one instance did it appear that an exothermic reaction occurred, as is illustrated by the curve which bends upward. This exothermic reaction occurred in an air-filled system. It is surprising that an exothermic reaction occurred with the air, whereas with the oxygen, no such exothermic reaction was observed. With oxygen, it appears the film apparently started to react, as evidenced by the fact that the curve does not decay as rapidly initially as that for a water film, and then for some unknown reason reaction ceased.

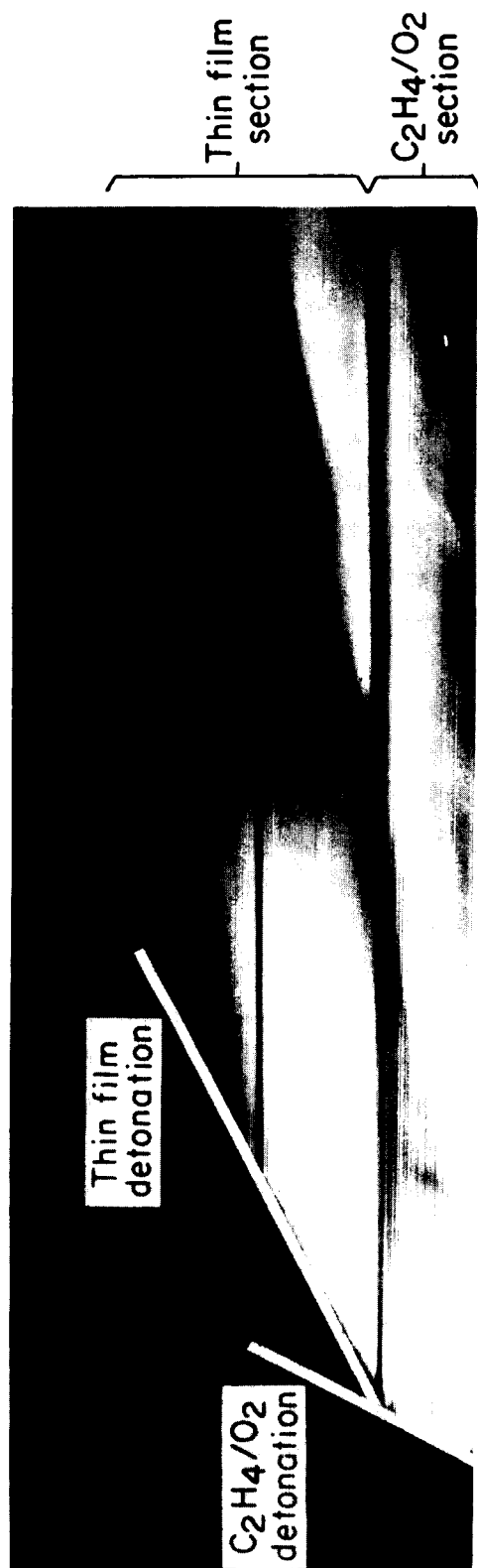


FIGURE 29. - Gas-Thin Film Studies; Typical Streak Camera Record.

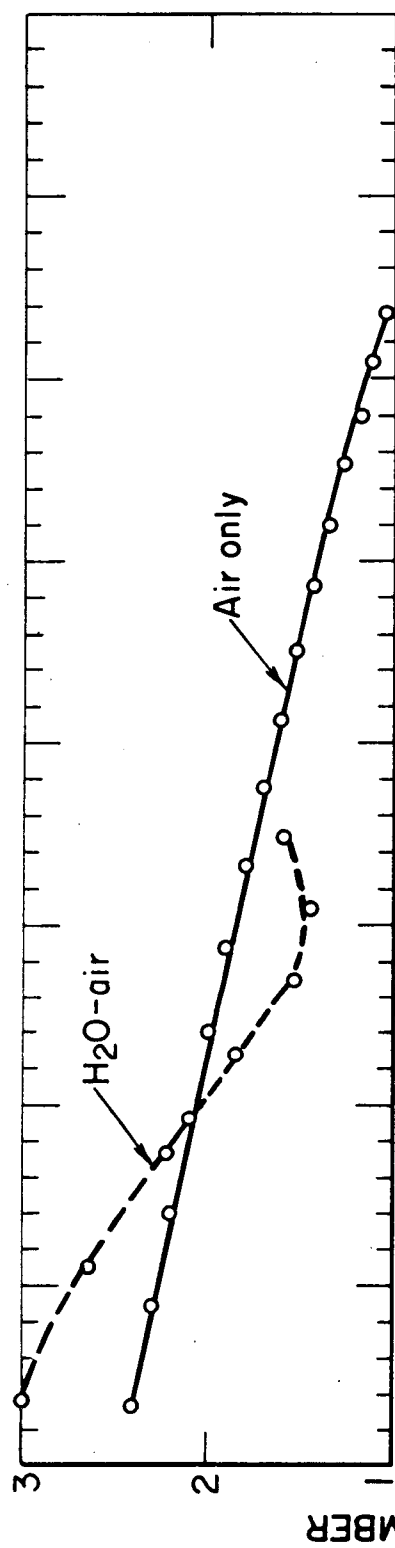


FIGURE 30. - Shock Mach Numbers in Gas-Thin Film Studies.

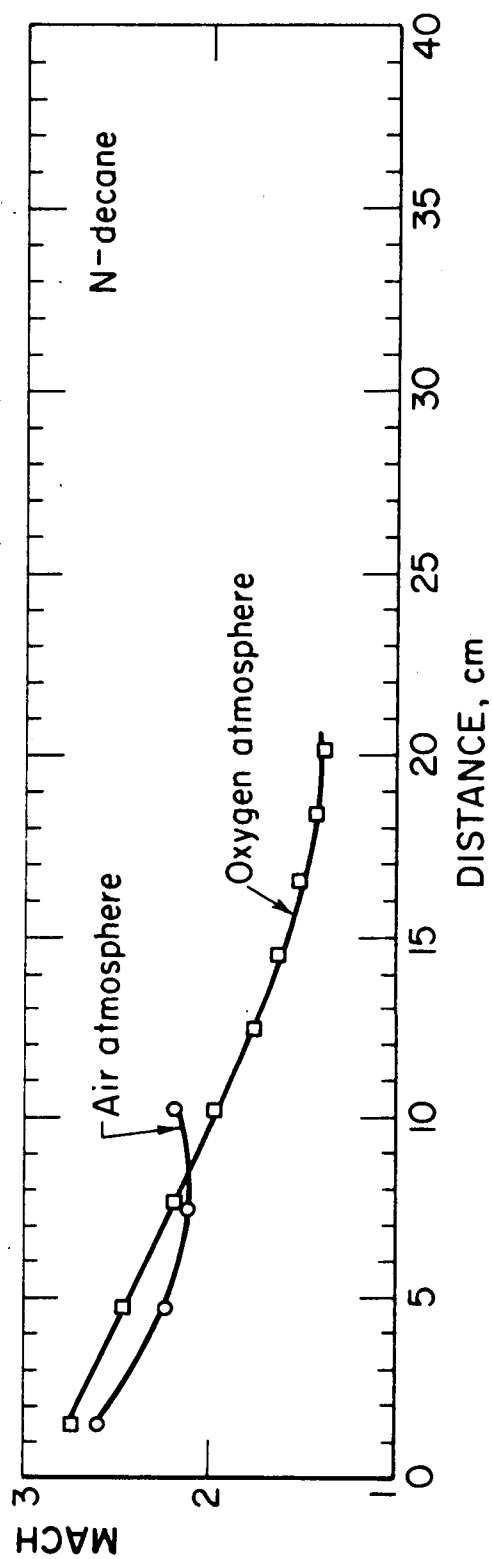
PGH-73
390

FIGURE 31. - Shock Mach Numbers in Gas-Thin Film Studies.

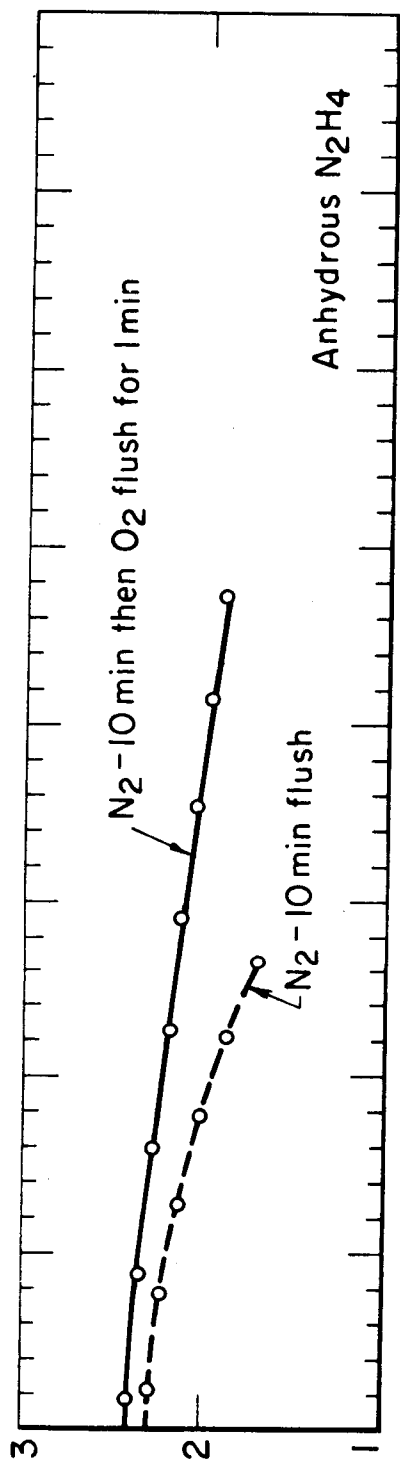


FIGURE 32. - Shock Mach Numbers in Gas-Thin Film Studies.

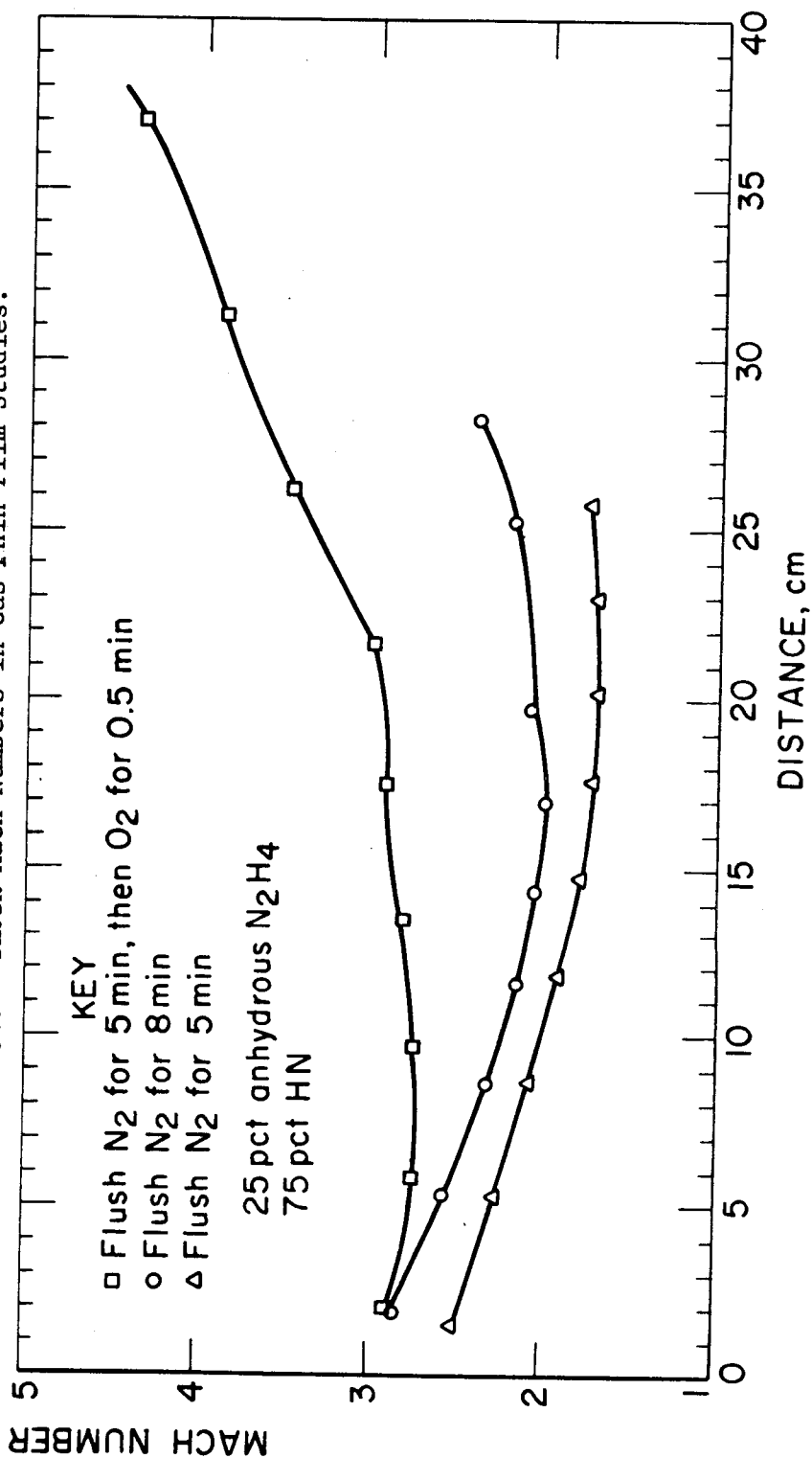


FIGURE 33. - Shock Mach Numbers in Gas-Thin Film Studies.

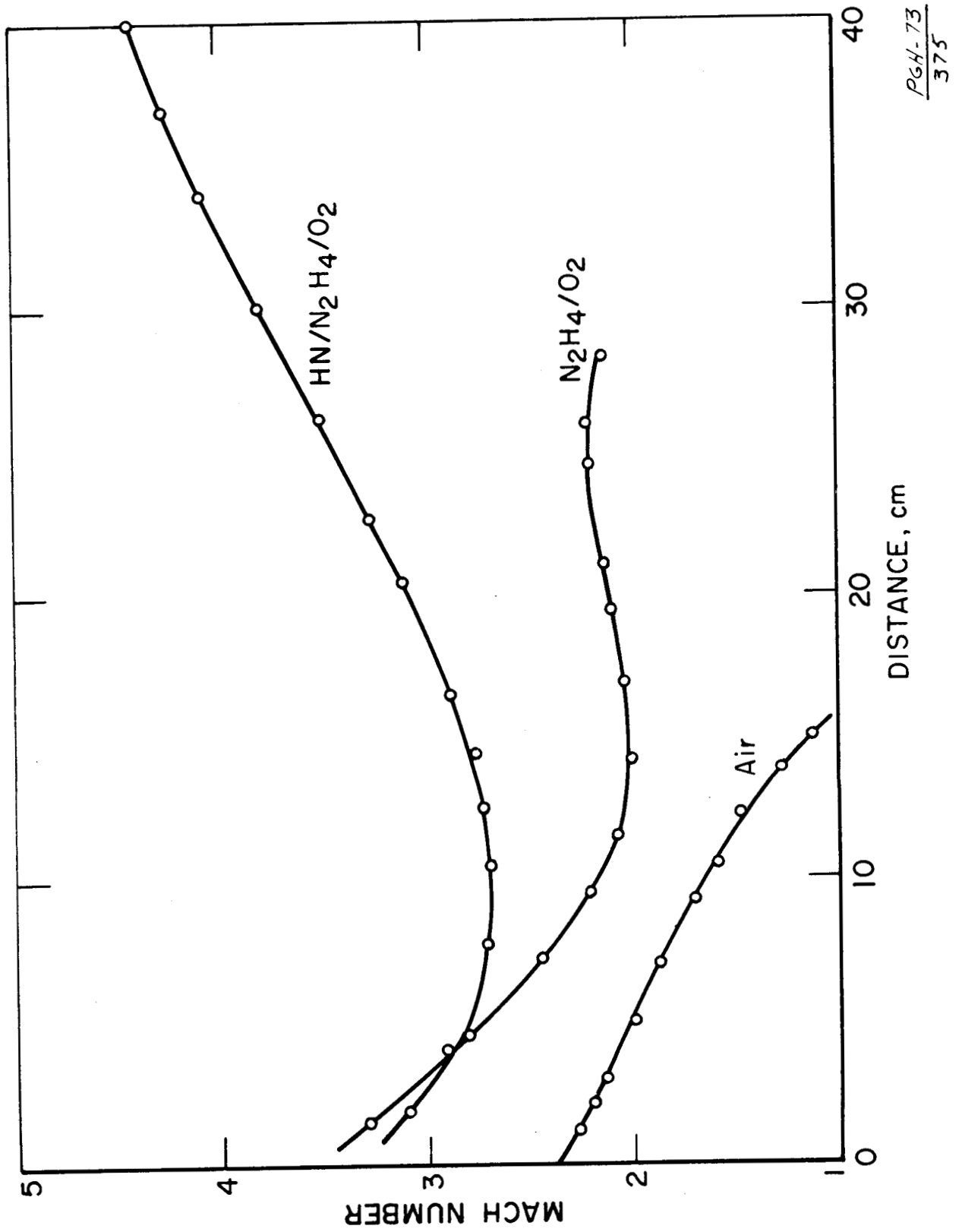


FIGURE 34. - Shock Mach Numbers in Gas-Thin Film Studies.

In the case of an anhydrous N_2H_4 film, two experiments were run; one in which pure nitrogen was used as the gas, and the other in which oxygen was used. In the runs using oxygen and N_2H_4 , it was necessary to first fill the tube with an inert gas (usually nitrogen) to minimize the reaction of N_2H_4 with oxygen, which is known to proceed at a fairly rapid rate. About 1 minute prior to initiation of the C_2H_4/O_2 mixture, the test chamber was quickly purged with oxygen. Although no attempts were made to analyze the N_2H_4 on the walls at the time of initiation, previous experience indicates that probably a fairly large amount of N_2H_4 was oxidized, forming nitrogen and water, so that the wall film consisted of a H_2O/N_2H_4 solution, and this is probably the reason that the Mach number decreased. However, the rate of decrease of the shock was much slower than that associated with the H_2O film, suggesting that some reaction occurred. Results are shown in figure 32. Figure 33 shows the results of experiments using a 75 pct HN/25 pct N_2H_4 solution as the film. Nitrogen was used in two of the runs, while in the third run a nitrogen flush was followed by an oxygen flush immediately prior to initiation. All these runs show a convex upward trend, indicating an exothermic reaction. Furthermore, even with the short-time oxygen flush, a Mach number of approximately 4.5 was obtained by the time the reaction front reached the end of the test chamber. This is an unexpectedly high value for a heterogeneous system.⁷

Gordeev et al. (38), Borisov et al. (39), and Rybanin (40) investigated the mechanism by which wall films contribute to a detonation process and explained this mechanism in the following manner. For relatively thin films (less than 0.5 mm), the shock passing over the film transmits a shock into the liquid that reflects from the tube wall and returns to the liquid surface, where it shatters the liquid and sprays it out into the region behind the shock. This process occurs so rapidly that the liquid drops are vaporized and burned within a few centimeters behind the incident shock and thereby are able to contribute to the forward motion of the shock front to help establish a detonation. For thick films (thicker than 0.5 mm), the shock reflection process apparently plays a minor role. The primary mechanism is the generation of aerodynamically induced waves in the liquid surface that rapidly reach such proportions that they disrupt the liquid surface and spew liquid into the region immediately behind the incident shock, which, as in the case of the thin film, vaporizes and burns so as to contribute to the forward motion of the shock. In our experiments, in which a HN/ N_2H_4 solution was used, it is also conceivable that a detonation might propagate through the HN/ N_2H_4 solution per se. This would explain the abnormally large Mach number observed in

⁷Figure 34 compares the results of experiments with HN and HN/ N_2H_4 solutions in an air atmosphere. The results for air only are also represented. The results for air in this figure are different than the results shown in figure 30, although the Mach number that is reached is the same. The difference in the two air traces is apparently due to the irreproducible nature of the C_2H_4/O_2 detonation process.

this experiment. Although the previously measured critical film thickness for this solution is 0.76 mm (table 4) for the high velocity detonation, it is possible that a low velocity detonation could propagate in these thin (0.07 mm) films.

These experiments demonstrate another mechanism by which the residues accumulated on RCS engine walls could contribute to an explosive combustion without detonation in the liquid film itself.

Summary

Many physical and explosion properties of HN and HN solutions were studied, both by the Bureau and by other investigators. Results of these studies are summarized here.

The heat of conversion from the β to the α form is 2 Kcal/mole HN. The infrared and x-ray spectra of HN were obtained. HN weight-loss rates were measured at elevated temperatures and reduced pressures. Results indicated that HN loss from the RCS engine through thermal dissociation and decomposition was not rapid enough to prevent the accumulation of hazardous amounts of the HN-rich residue.

The densities for given concentrations of HN in either hydrazine or water are satisfactorily represented by the equation $\rho = \rho_0 + aN + bN^{1/2}$. Similarly, the expressions describing the kinematic viscosity as a function of absolute temperature and HN concentration in hydrazine and water are $\log_{10} \frac{\nu}{\nu_0} = K \frac{N}{T}$ and $\log_{10} \frac{\nu}{\nu_0} = K \frac{N^2}{T}$, respectively. The surface tensions of molten HN and various HN/N₂H₄ and HN/H₂O solutions at elevated temperatures were measured and found to be satisfactorily represented by the expression, $\gamma = \gamma_0 + (K_1C - K_2) \cdot (T - T_0)$.

HN was found to decompose explosively at about 300° C. The detonation velocity for a pure molten HN film at 75° C was found to be 8,500 m/sec, which agrees with the values obtained by other investigators using cylindrical charges. The ballistic mortar showed a TNT equivalence of 142 for HN. Impact sensitivity tests gave 50-pct probability for ignition at drop-weight heights of 175 kg-cm for cup and plunger, and 50 kg-cm for ERL type 12 tool test procedures.

Thin-film detonation studies have shown that molten HN, or HN/N₂H₄ and HN/H₂O solutions having HN concentrations of at least 40 and 75 pct, respectively, exhibit stable detonations; HN/N₂H₄ and HN/H₂O solutions containing 20 and 65 weight percent HN or less, respectively, do not support stable detonations.

HN, HN/N₂H₄, and HN/A-50 solutions were found to be incompatible with NTO; although considerable reaction was evident, none of the reactions approached an explosive magnitude. Other investigators have reported

detonative reactions of HN with cobalt and nickel. In similar experiments, the Bureau found no violent reaction when heated molybdenum chips were dropped into molten HN.

A shock from an C_2H_4/O_2 detonation (with the C_2H_4/O_2 mixture initially at 1 atm) was not sufficient to initiate detonation in HN/ N_2H_4 solutions containing as much as 75 pct HN; however, the hot products from such a gas-phase detonation apparently initiated a detonation in the mixture. Cavitation of the HN/ N_2H_4 solution did not affect these results to any measurable degree.

Pure granular and molten HN were detonated when subjected to shock pressures of higher magnitude, equal to or larger than 500 atm, which were generated by a stoichiometric C_2H_4/O_2 detonation.

HYDRAZINE DINITRATE (H2N)

Introduction

Another material believed to be present in the engine residue is hydrazine dinitrate (H2N). H2N is known to decompose easily, even at low temperatures. Its major decomposition products are HN, ammonium nitrate (AN), and hydrogen azide (N_3H). The azide is a sensitive material. Thus, H2N was studied as a possible source of explosive reactions and its properties, essential to understanding the explosive characteristics of engine residues, were measured.

The H2N used in these tests was prepared by the Bureau from HN and concentrated nitric acid. H2N, which precipitates in excess nitric acid, was filtered and washed thoroughly with ether or chloroform, and then dried in a vacuum desiccator. The purified material contained more than 99 pct H2N.

Physical Properties of H2N

X-ray and Infrared Spectra

X-ray diffraction studies of H2N were hampered by its highly hygroscopic nature. The principal lines of the x-ray spectrum, obtained by the Bureau, are shown in table 8.

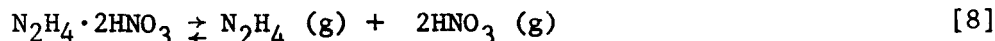
TABLE 8. - X-ray diffraction spectrum for H2N

d, Å	I/I ₀	d, Å	I/I ₀
4.82	25.8	2.41	61.4
4.72	25.9	2.18	27.0
4.31	12.7	2.05	11.1
4.12	18.9	2.01	15.9
4.05	36.0	1.99	14.5
3.97	13.4	1.97	15.6
3.89	39.2	1.90	10.1
3.59	100.0	1.85	14.2
3.57	97.8	1.80	12.9
3.37	38.1	1.73	8.9
3.30	82.6	1.61	35.0
2.84	33.3	1.52	11.8
2.80	28.8	1.39	12.6
2.74	22.1	1.34	11.2
2.64	35.3	1.29	13.5
2.43	41.0		

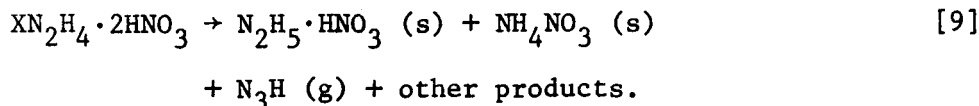
The most useful signature of the various materials of interest to the Bureau program was that of the infrared spectra. Unfortunately, H2N is a highly reactive acidic salt, incompatible with many of the materials used in the preparation of samples for infrared spectral analysis. The best spectrum of H2N, prepared with KBr, is shown in figure 35.

Dissociation and Decomposition (Weight Loss Rate)

As in the case of HN, studies were also conducted with H2N to measure the temperature and pressure dependence of its dissociation (or decomposition). H2N dissociates according to the reversible reaction



and decomposes according to the irreversible reaction



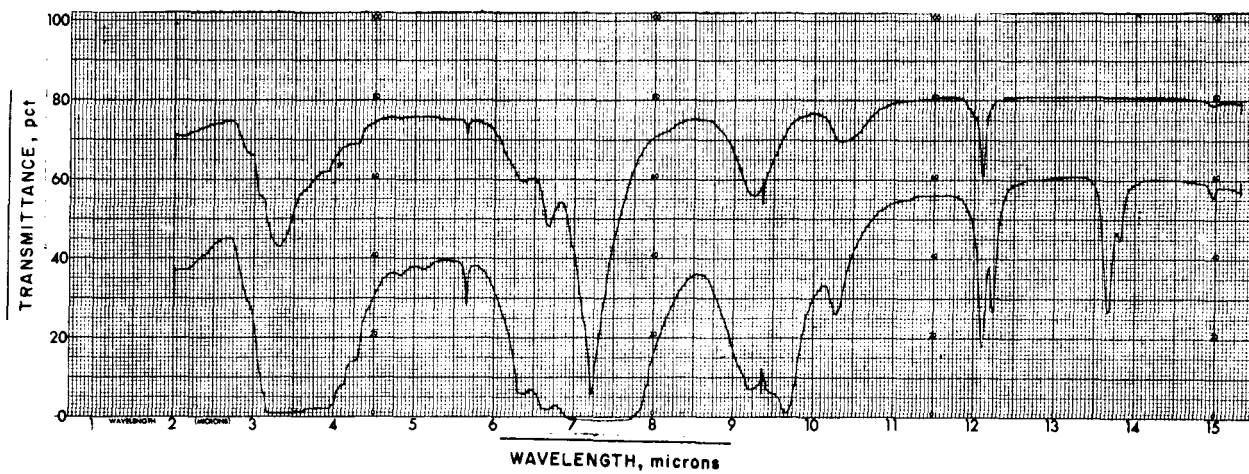


FIGURE 35. - Infrared Spectrum of H₂N.

H₂N, unlike HN, exhibited a measurable mass loss rate at temperatures below its melting point. H₂N melts at 103° to 104° C when heated rapidly; when heated slowly, it begins to decompose without melting at approximately 80° C. The weight loss of H₂N at 25° C is shown in figure 36. Mass loss experiments of H₂N were conducted in the same manner and with the same experimental apparatus as previously described for the HN studies (quartz spring balance). Except at temperatures below its melting point, where the weight loss was a linear function of time, as shown in figure 36, the weight loss rate was nonlinear and was normally characterized by a rapidly decreasing rate, as illustrated in figure 37. This decreasing rate is apparently due to the change in chemical composition of the sample. As dissociation of the H₂N proceeds, it breaks down into other solids such as AN and HN, which slow down further dissociation. The runs shown in figures 36 and 37 were both carried out at 200 μ Hg and 25° C and 75° C, respectively.

The dissociation/decomposition of H₂N was of particular significance to this investigation for two reasons; N₃H, a very unstable explosive gas, is cited in the literature as one of the products of decomposition; also, although the thermal decomposition of H₂N is sufficiently rapid, making its residence time in the engine short, its solid decomposition products AN and HN, themselves explosives, are not as easily decomposed and are retained in the engine.

In the Bureau measurements of the mass loss rate of H₂N, no attempt was made to determine the quantitative contribution of dissociation to the total mass loss rate. According to Sabanejeff (8), when H₂N is heated slowly, it begins to decompose, without melting, at ~ 80° C and yields, in addition to other minor products, N₃H, nitric acid, nitrogen and water, leaving a residue of HN and AN.

Sabanejeff (8) found that a one-half gram sample of H₂N, when heated to 80° to 85° C, lost 59 pct of its weight. When he heated a sample in a water bath at 100° C, almost all the sample decomposed, leaving a small residue of AN.

$$\frac{P_{CH-73}}{376}$$

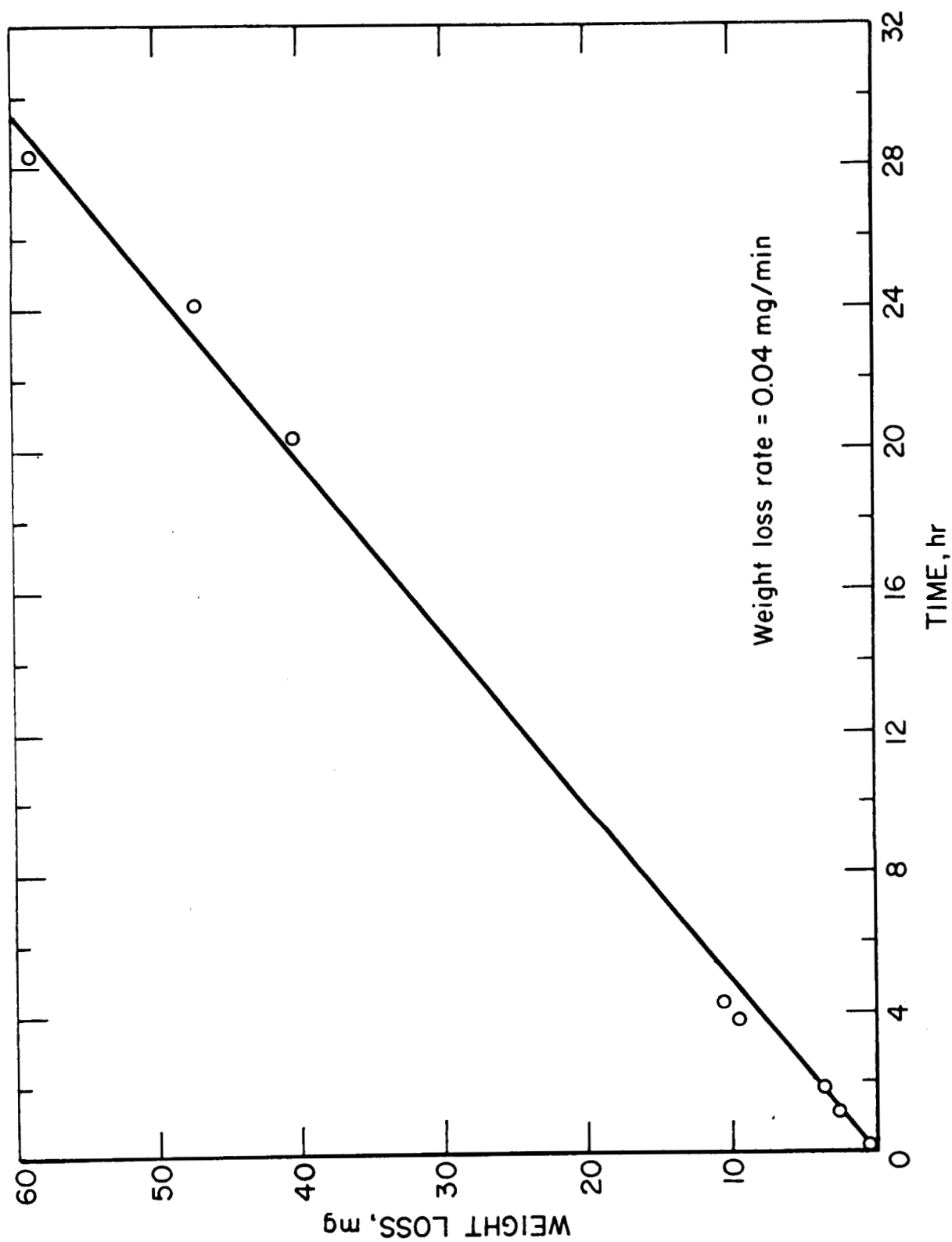
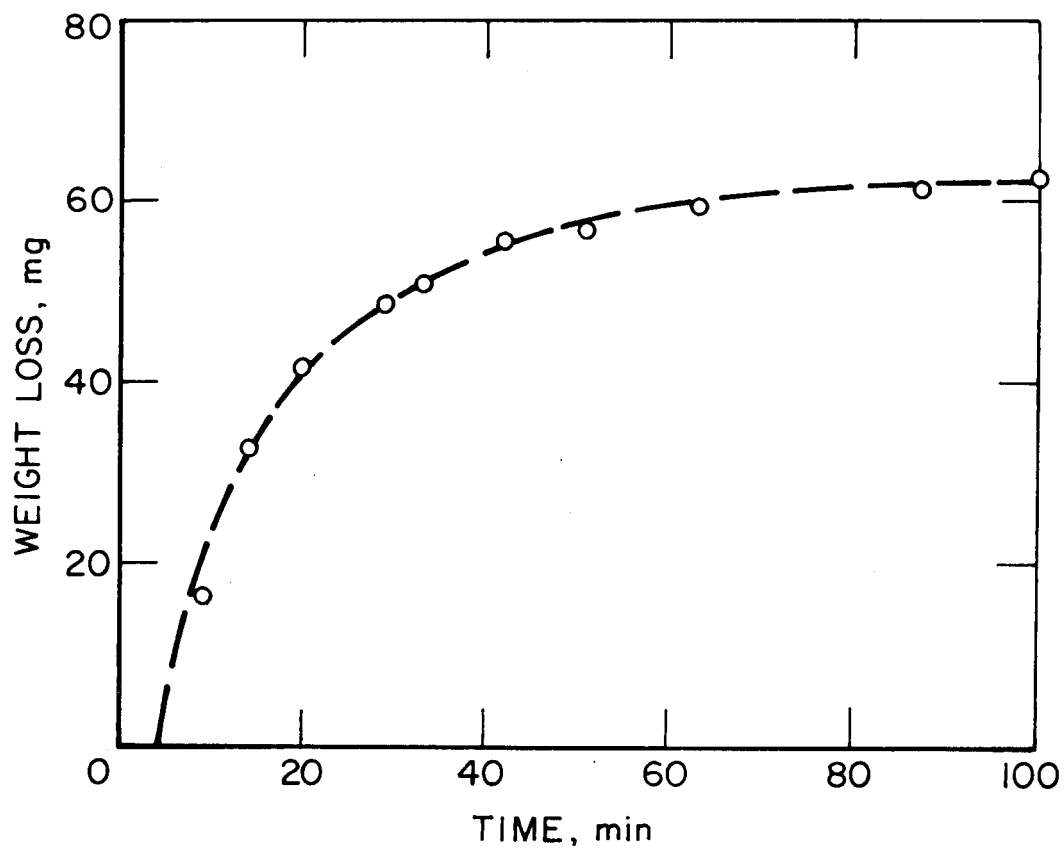


FIGURE 36. - Weight Loss of H₂N at 25° C and at 200 μ Hg.



PGH-13
377

FIGURE 37. - Weight Loss of H₂N at 75° and at 200 μ Hg.

In the tests performed by the Bureau, the rate of decomposition of H_2N was measured at four temperatures at a pressure of 200 μ Hg. Close observation of the decomposing H_2N showed it to retain its granular structure at low temperatures during decomposition; at higher temperatures, and notably those in the vicinity of 80°C , it was found that the sample underwent a physical change. The material appeared to be semifluid, exhibiting a bubbling process, similar to that of boiling liquids; however, the surface retained a crusty appearance and the mass remained opaque. Apparently the mass, which consists of undecomposed H_2N , HN , and AN , becomes more and more enriched with HN and AN especially on the surface. HN and AN together dissociate slowly at this temperature, even though it is above the melting point of pure HN . The upper crust impeded the dissociation of H_2N and slowed it down until it asymptotically approached that corresponding to the AN/HN mixture. This is apparently the case for the results shown in figure 37 where the rate of mass loss decreases from an initial value of approximately 2.8 mg/min to a value of 0.05 mg/min after 100 min. Table 9 summarizes the results of these experiments.

TABLE 9. - Decomposition of H_2N ; summary of results

Initial weight of sample, grams	Initial weight loss rate, mg/sec	Pressure range, microns Hg	Temperature, $^\circ\text{C}$	Reciprocal temperature, $1/^\circ\text{K}$	Percent initial weight loss rate, sec^{-1}
0.2579	0.00057	230 to 170	25	0.00336	0.22
.2359	.0026	95 to 120	38	.00322	1.12
.3101	.011	200 to 220	60	.0030	3.62
.2377	.046	215 to 205	76	.00287	19.25
.2025	.047	190 to 140	78	.00285	23.29

Figure 38 shows a plot of the logarithm of the percent of initial (maximum) weight loss rate of H_2N as a function of the reciprocal of the absolute temperature. The linearity of the curve in such a coordinate system suggests that the reaction is primarily a decomposition. This agrees well with the visual observations during the testing periods; no deposits of recombined dissociation products were found on the colder areas of the apparatus. Deposition was observed on the walls when the tests were done with the dissociating HN . Thus, we conclude that H_2N undergoes decomposition when heated.

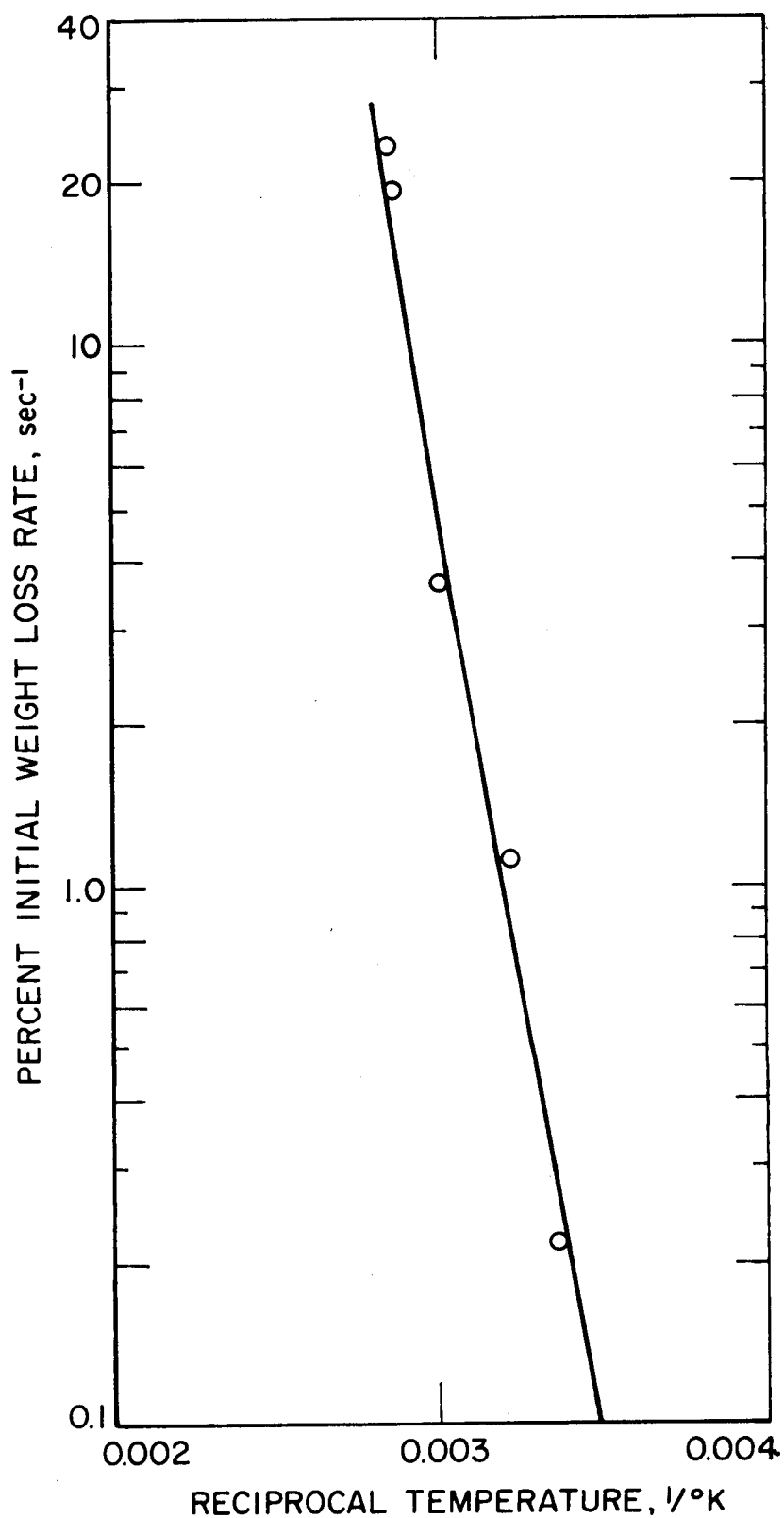


FIGURE 38. - Percent Initial Weight Loss Rate of H_2N as a Function of the Reciprocal Temperature at $200 \mu \text{Hg}$.

At temperatures greater than 80° C, the mass loss rate was too rapid to record with the available instruments. From such plots as the one in figure 38, an activation energy for the process was calculated to be 11 cal/g-mole of H₂N. The mass loss rate of H₂N cannot be compared with that of HN because the HN mass loss below 250° C and at low pressures follows a dissociation mechanism, and is consequently proportional to the exposed surface area of the sample; whereas for the H₂N, it appears to be a decomposition mechanism and consequently proportional to total mass.

Comparing Sabanejeff's (8) mass loss results with the Bureau's at 80° C, shows the former's 300-min run versus the Bureau's 100-min run gave weight losses at 39.6 and 41.2, respectively, and in good agreement. Apparently, most of the decomposition is completed within the shorter period of 100 min.

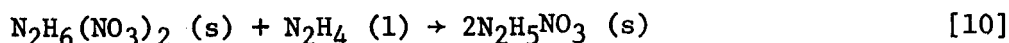
As noted above, the azide formation in the decomposition of H₂N was of major interest. Sabanejeff (8) studied the decomposition of H₂N over sulfuric acid at room temperature in a desiccator and found that the gaseous product was mainly N₃H. Bureau experiments revealed that the gases collected (in a desiccator) as a result of the spontaneous decomposition of H₂N, initially at vacuum and at room temperature, consisted of 55 pct N₂, 40 pct N₂O, 1 pct O₂, and 5 pct CO₂; N₃H and water were not detected. The CO₂ may have come from the drying agent in the desiccator. The gases evolved during thermal decomposition of H₂N in a helium atmosphere (220 mm Hg) consisted of 50 pct N₂, 35 pct N₂O, 13 pct H₂O and less than 1 pct each of N₃H and O₂. To minimize loss due to possible leaks, and to decrease the surface area of glassware exposed to the gases as well as to shorten the time between decomposition and testing of the gases evolved, the evacuated glass flask containing the sample of H₂N was directly connected to a mass spectrometer and then heated. Prior to heating, only water vapor was evolved. At 75° C, the gases detected by the mass spectrometer, exclusive of water vapor, were 63 pct N₂, 28 pct N₂O, 9 pct NO, 0.1 pct N₃H, and trace amounts of O₂. Only small amounts of N₃H, if at all, were detected in the Bureau tests, in contrast to the results quoted by Sabanejeff. N₃H is very reactive; it is strongly adsorbed on glass (41), displacing the water in the glass; thus the type of glass used in the tests, its pretreatment, and time of contact between gas and glass can all influence the results. The glassware used by the Bureau was not pretreated with N₃H. Sabanejeff does not mention the condition of his apparatus.

Chemical Properties of H₂N

Reaction of H₂N with N₂H₄

In the course of the MSC's RCS engine qualification program, they observed an occasional anomalous combustion chamber temperature history during repetitive firing of the engine for a certain number of pulses followed by a short interval of nonpulsing. After the expected smooth rise in temperature, there occurred a lowering of the temperature, followed again by a

rise in temperature, this time to a somewhat higher degree and so on.⁸ Since this behavior appeared to be associated with an exothermic reaction, some thought was given to the various types of exothermic reactions likely to occur in these engines. One of these concerned the reaction of H₂N with liquid N₂H₄ to form HN according to the reaction



Preliminary investigation of this reaction indicated that it evolved considerable heat and released small amounts of gases. The gases evolved during the reaction were collected and analyzed by mass spectroscopy and the results were as follows:

<u>Gas detected</u>	<u>Percent in sample</u>
N ₂ O	4.7
N ₂ H ₄	5.0
N ₂	80.6
H ₂ O	5.3
NH ₃	2.0
N ₃ H	0.1
Unidentified	2.2

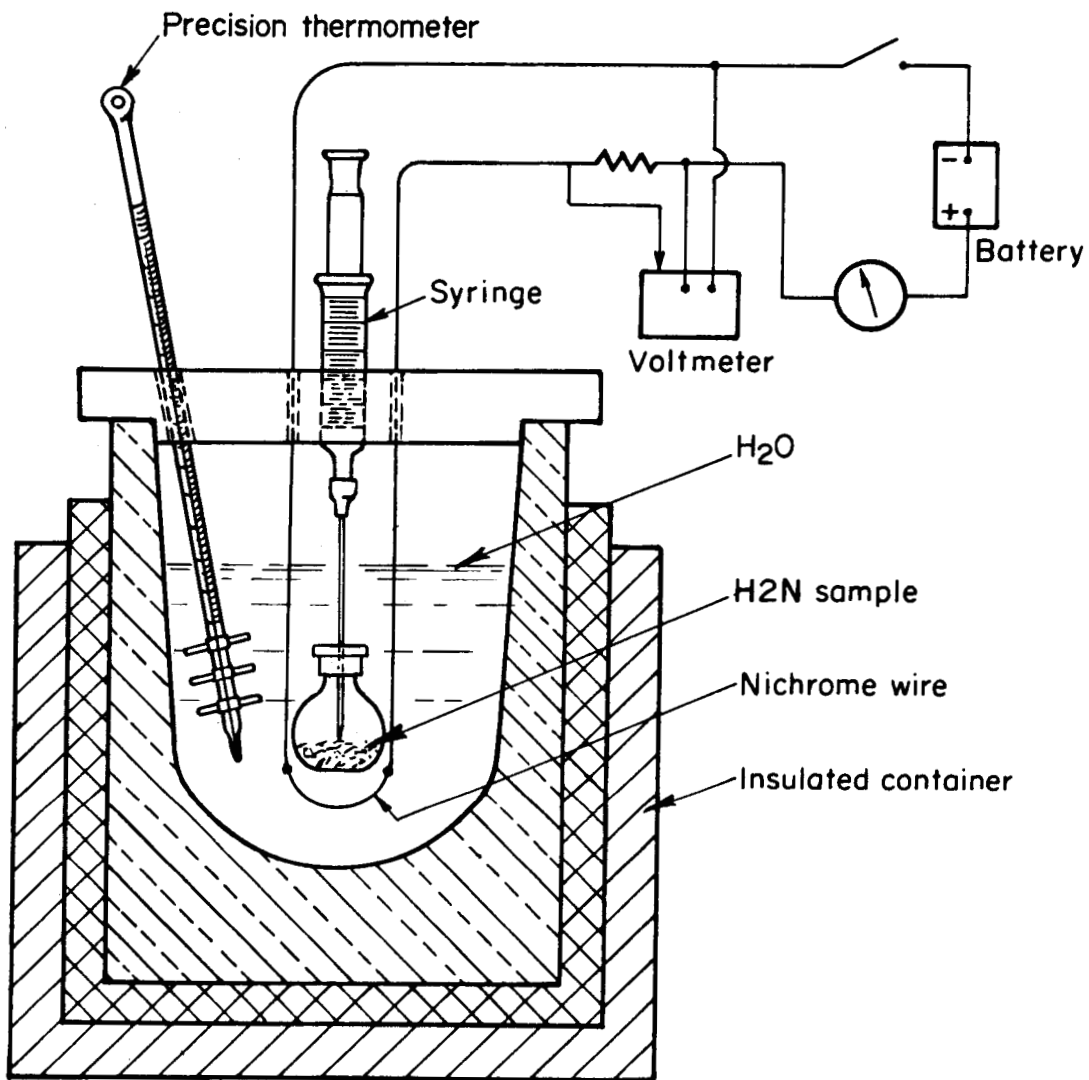
The amount of gas constituted only about 0.1 pct of the original sample, by weight. The results suggest that decomposition of the H₂N occurs during the reaction, probably as a result of the thermal energy released, though to a very small degree.

The heat of the reaction between H₂N and N₂H₄ was measured in the calorimeter (fig 39). The calorimeter was calibrated with the nichrome⁹ resistance wire by heating the wire with a known current and voltage for various lengths of time and measuring the temperature rise. During calibration, HN was placed in the small glass vial to account for the heat capacity of the reaction product. A weighed amount of solid reactant was placed in the glass vial and a stoichiometric amount of liquid N₂H₄ was drawn into the syringe; the apparatus was assembled as shown in the figure. The average heat evolved in three runs was 15±1 Kcal/g-mole of H₂N at 25° C, compared to a calculated value of 19 Kcal/g-mole¹⁰ of H₂N. The calculated and experimental values do not agree too well. The calculated value does not account for the decomposition of H₂N that possibly takes place, and consequently is expected to be somewhat higher. Other sources of error may be due to a small amount of N₂H₄ having remained in the needle of the syringe or to the heat of reaction bringing about some decomposition of the hydrazine not yet reacted. With an engine that weighs about 450 grams, 1 gram of H₂N reacting with N₂H₄ will increase the temperature by about 2° C.

⁸The temperature-time plot had a saw-tooth profile.

⁹See footnote ⁴ on page 32.

¹⁰Calculated from bond energies and heats of formation.



PGH-73
379

FIGURE 39. - Calorimeter Used in the Measurement of Heat of Reaction of H_2N with N_2H_4 .

Reaction of H₂N With NTO

H₂N was dropped into liquid NTO to determine if the material would detonate. Although the reaction was extremely fast, there was no apparent tendency for the material to explode for the 10-gram sample tested.

Explosion Characteristics of H₂N

TNT Equivalence and Impact Sensitivity

The TNT equivalence and impact sensitivity of H₂N were determined in the same manner and the same equipment as previously used in the HN measurements. A TNT equivalence of 75 pct was found; an impact sensitivity of 115 Kg-cm and 65 Kg-cm were obtained for the cup-and-plunger and sandpaper tests,¹¹ respectively. It is of interest that the TNT equivalence of H₂N is approximately one-half that of HN, furthermore, H₂N appears to be less sensitive to shock impact than HN. This fact was unexpected, since we had anticipated the dinitrate to be less stable than the mononitrate.

Summary

X-ray and infrared spectra for H₂N were obtained. The reaction of H₂N with N₂H₄ was found to proceed with a heat of reaction equivalent to about -15 Kcal/g-mole of H₂N at 25° C. This reaction was accompanied by release of the gases N₂O, N₂, H₂O, NH₃, and N₃H. Reaction of H₂N with liquid NTO, although very fast, was not explosive.

H₂N was found to have a TNT equivalence of 75 pct and an impact sensitivity of 115 Kg-cm and 65 Kg-cm for the cup-and-plunger and sandpaper tests, respectively.

H₂N decomposes when heated in a vacuum and gives off mainly N₂, N₂O, NO, and H₂O, with the respective concentrations dependent on the temperature of decomposition. Traces of O₂ and N₃H were detected in some of the runs. The undecomposed portion contained, in addition to H₂N, a mixture of HN and AN. The decomposition gases were studied in detail, because they were reported to contain large amounts of N₃H. However, only trace amounts of this gas were observed in the Bureau tests. But even trace amounts are undesirable in the RCS engines; the solid decomposition products, namely AN and HN, also are undesirable.

Thus, although H₂N easily decomposes and can be removed by thermal means, its presence in engine residues is not desirable.

¹¹These are standard tests for measuring the impact sensitivity of explosives, and were used in testing HN and any of the other materials prepared in this program that were tested for impact sensitivity.

HYDRAZINE NITRITE

Introduction

Hydrazine nitrite also was suggested as a possible constituent of the engine residue. Although the nitrite was found in the product from the flow reactor used in Bureau studies (see volume IV), it was not detected in the MSC RCS engine residues analyzed by the Bureau. These results, however, are not unexpected. The nitrite decomposes very easily, even at room temperature. Trace contaminants also accelerate the decomposition of the nitrite, and the samples from the MSC RCS engines were not analyzed immediately after sampling; shipping time (to the Bureau) took several days.

Hydrazine nitrite is reported to be a sensitive explosive (42). Ammonium nitrite, a substance similar in properties to hydrazine nitrite (43), is known to decompose explosively at relatively low temperatures.

We were unsuccessful in preparing enough nitrite for the various tests for explosive sensitivity and combustion characteristics. Only small amounts of nitrite were obtained when the hydrazine nitrite was prepared according to a method suggested by Sommer (44) and the purity of the salt was not established. No other preparation procedure was found in the literature.

Physical Characteristics

Hydrazine nitrite was obtained from the reaction of hydrazine sulfate and barium nitrite in a water solution. The purity of the resultant salt was never satisfactorily determined. Different analytical techniques gave different results. The presence of nitrite was shown, and it was verified, by atomic absorption spectroscopy, that the product did not contain barium.

The melting point of the material was measured in a DSC to be 42° C, in agreement with the value cited by Sommer (44). The infrared spectrum measured at the Bureau is shown in figure 40. An attempt to obtain an x-ray spectrum was unsuccessful. DSC studies, in the range from -20° to 350° C showed many peaks and thermal changes, even at low temperatures, indicating reactions at these low temperatures. Due to its chemical instability, no further work was done on this compound.

Sommer (44) postulated that hydrazine nitrite decomposes according to the reaction:



with the reaction being catalyzed by nitrous acid. Nitrous acid is conceivably formed in the RCS engine as a result of a reaction between NTO and H₂O, and was found in products from reactions taking place in the 2-D engine and the gas flow reactor. Therefore, the possibility of hydrazine nitrite accumulating in the engine residues is poor.

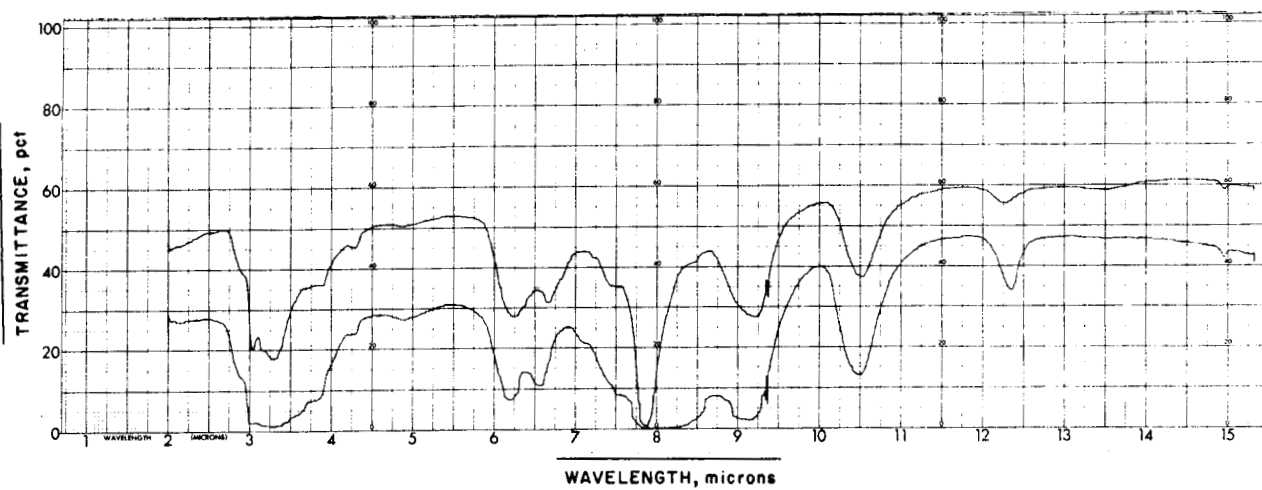


FIGURE 40. - Infrared Spectrum of Hydrazine Nitrite.

MONOMETHYLHYDRAZINE NITRATE (MN)

Introduction

It has been noted that fewer pressure spikes or hard starts occur with the monomethylhydrazine (MMH)/NTO propellant system than with the N_2H_4 /NTO or A-50/NTO systems. Conceivably, the reaction products of the MMH/NTO combination which accumulate in the residues are not sensitive. For this reason, it is of value to compare these products with those from the N_2H_4 /NTO or A-50/NTO reactions.

The main product of the MMH/NTO reaction was monomethylhydrazine nitrate (MN); it was also found in residues from pulse-mode-fired 1-lb thrust motor tests (45) as well as in the products of MMH/NTO reactions studied by Seamans and Dawson (46), Mayer and his coworkers (47), and the Bureau of Mines, as reported in volume IV of this report. Zung and Breen (48) reported AN, instead of MN, to be the major product of the reaction in their studies. AN also was found in combustion products of a pulse-mode-fired 22-lb thrust engine and of a steady state fired 1-lb thrust motor (45).

The MN used in our investigations was prepared in the same manner as was HN; but since MN does not precipitate upon addition of nitric acid to the methanol solution of MMH, the solution is evaporated in vacuum and gently heated until MN precipitates. The salt is purified by melting in warm methanol followed by crystallization. MN was found to be 98.5 pct pure.

Physical Properties of MN

Infrared and X-ray Spectra

The infrared spectrum of the pure MN salt, pressed in a KBr pellet, is shown in figure 41. The x-ray spectral lines for MN are given in table 10.

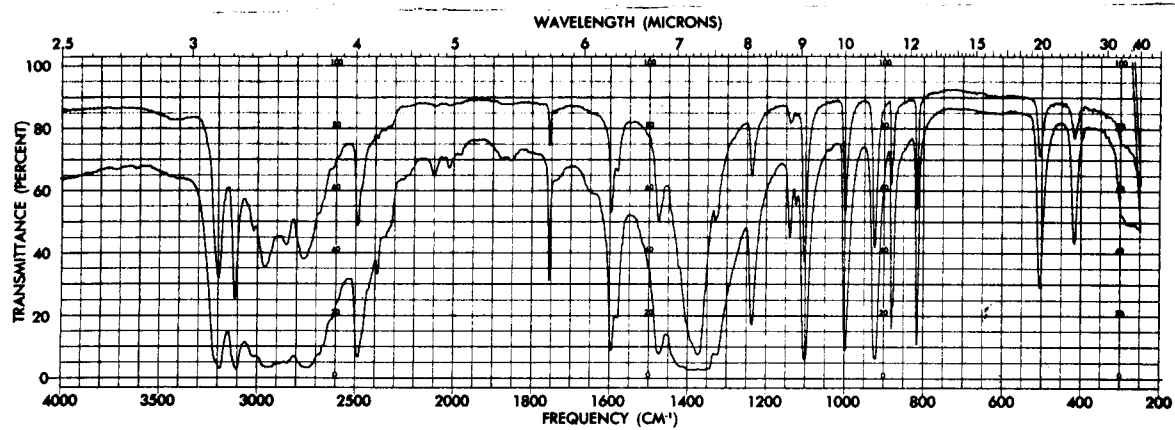


FIGURE 41. - Infrared Spectrum of MN.

TABLE 10. - X-ray diffraction spectrum of MN
(results of Bureau of Mines
analysis)

d, Å	I/I ₀
7.87	86.3
5.5	25.6
5.02	27.2
4.37	22.8
3.93	59.5
3.39	51.8
3.10	100.0
2.88	52.6
2.79	42.4
2.68	14.8
2.59	18.3
2.47	10.7
2.38	26.0
2.26	20.1
2.23	25.0
2.17	14.8
1.87	18.5

Thermal Properties

The melting point of MN as measured in the DSC by the Bureau was found to be 41.5° C. There was indication of boiling or dissociation starting at 120° C. A thermogram of MN is shown in figure 42. Both Mayer and coworkers (47) and Takimoto and Denault (45) have studied MMH/N₂O₄ reactions and their products in detail. The thermograms of their reaction products (residue) and of MN prepared by the latter are reproduced in figures 43 and 44, respectively. In figure 44, it is seen that boiling and/or slow decomposition of the MN prepared by Takimoto and Denault (45) starts at about 180° C, a temperature higher than found by the Bureau by 60° C. Although phase change temperatures are dependent to an extent on the heating rate, a difference of 60° C in the results cannot be attributed to differences in the heating rates. Peak temperatures concur.

Mass Loss Rate

A few determinations were made of MN mass loss rates. At low pressures, MN dissociated rapidly and the gaseous dissociation products recombined and deposited on available cold surfaces inside the test apparatus (quartz spring balance). Results of mass loss rate measurements at 25°, 55°, and 94° C, all at low pressures, were as follows:

Test temperature, °C	Pressure, microns Hg	Mass loss rate, mg/min ⁻¹ cm ⁻²
25	35	0
55	25-30	0.04
94	25-30	.35

MN, like HN, exhibits no measurable dissociation at temperatures below its melting point, and its rate of dissociation increases with increased temperatures.

Explosion Characteristics of MN

Detonation Behavior

The detonation characteristics of MN and solutions of MN in MMH and in water were measured by the Bureau, and it was found that even very concentrated solutions containing 90 pct MN did not sustain detonation in layers as thick as 1.25 cm. The pure molten MN showed low velocity detonation behavior with a detonation velocity of 2,200 m/sec, and a critical film thickness of 0.03 cm.

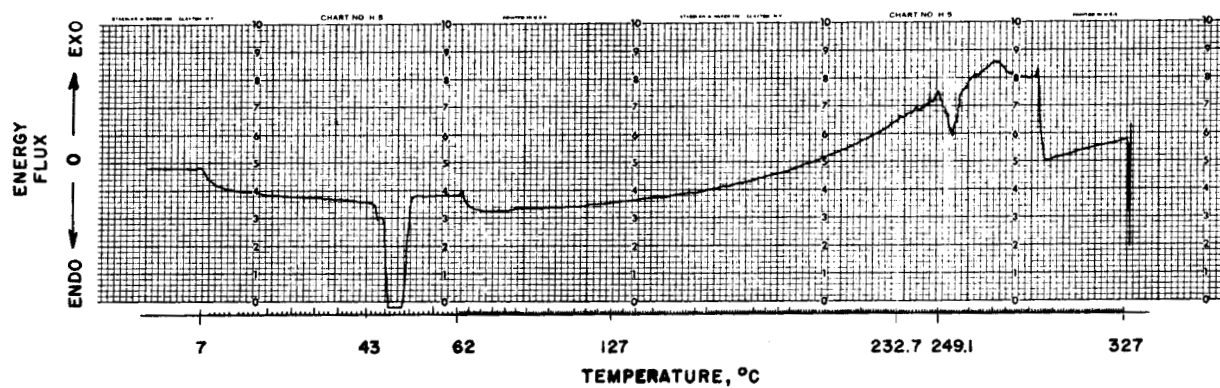
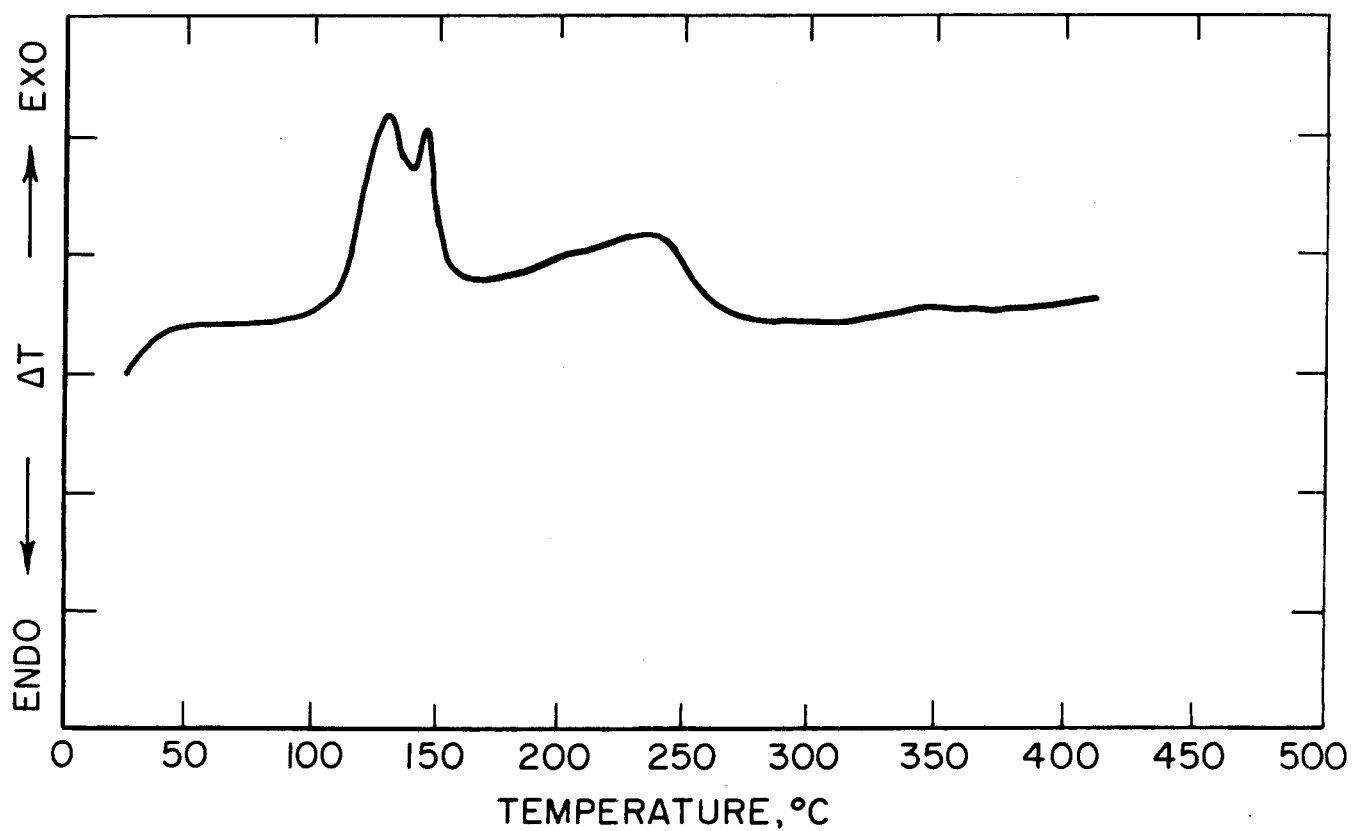


FIGURE 42. - Differential Scanning Calorimeter Record of MN.



P6H-13
380

FIGURE 43. - A differential Thermal Analysis Curve (Thermogram) for Residue from MMH/HNO₃ Reaction. [From Mayer, Taylor and Schieler (47)]

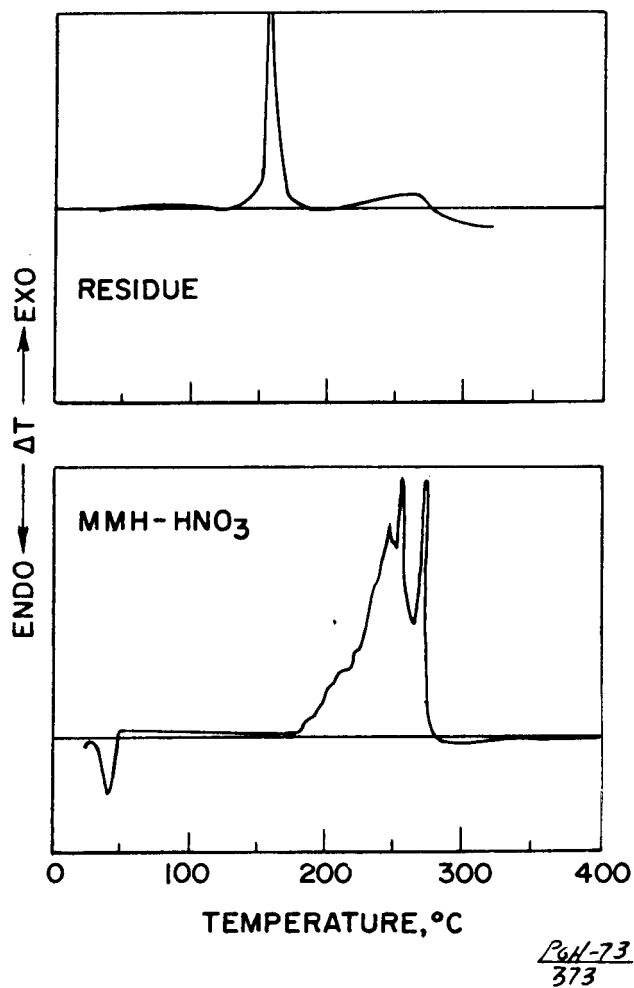


FIGURE 44. - A Differential Thermogram of MN (from Takimoto and Denault (45)).

TNT Equivalence and Impact Sensitivity

The TNT equivalence and the impact sensitivity of MN also were measured and found to be 136 pct and 77.5 Kg-cm, respectively. A value of 71.3 Kg-cm for impact sensitivity of MN was obtained by Seamans and Dawson (24).

Heating Effects on MN

When MN in the semisolid form of the engine residue was heated at 170° C and at atmospheric conditions, it converted to methylamine nitrate (45). On the other hand, when it was heated in vacuum, it dissociated into MMH and HNO_3 and recombined on cold surfaces. AN behaves in similar fashion, with the mode of decomposition being a function of the pressure. Thus, the possibility of methylamine nitrate forming in actual flight conditions in deep space at very low pressures is small.

FORMATION OF MONOMETHYLHYDRAZINE DINITRATE (M2N)

MN, when combined with excess nitric acid, will form monomethylhydrazine dinitrate (M2N). M2N was prepared by Takimoto and Denault (45), who obtained its infrared spectrum and differential thermogram. It is possible that MN, when present in the residue on the engine walls, will react with injected NTO to form M2N. M2N decomposes at a lower temperature than does MN, as seen in the differential thermogram, obtained by Takimoto (45), and reproduced in figure 45.

UNSYMMETRICAL DIMETHYLHYDRAZINE NITRATE (UN)

Introduction

HN is a major constituent of the engine residues when N_2H_4 is the fuel used; MN is often contained in the residues when MMH is the fuel. Therefore, it was expected that unsymmetrical dimethylhydrazine nitrate (UN) would be a major constituent of the engine residues when UDMH (unsymmetrical dimethylhydrazine) was the fuel; likewise it was expected that if the fuel were A-50 (a 50:50 mixture of N_2H_4 and UDMH), a mixture of HN and UN would be found in the residue.

However, this was not found to be the case in the Bureau of Mines experiments. No UN was detected in RCS engine residues or in the reaction products of the 2-D plastic engine; in one or two of the flow reactor products of reaction described in volume IV of this report, very small amounts of UN mixed with AN were observed.

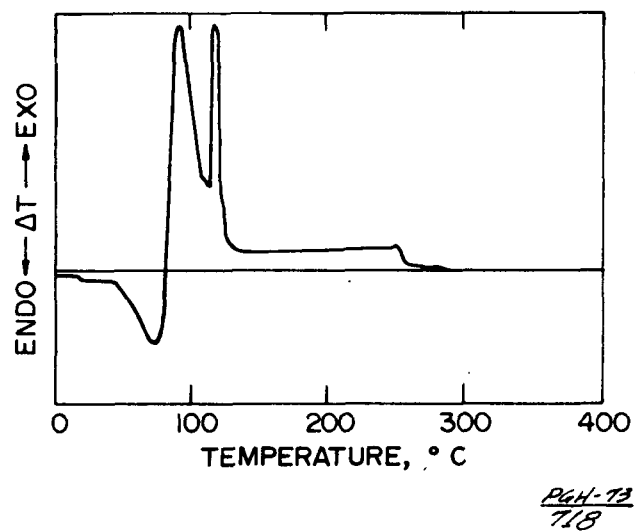


FIGURE 45. - A Differential Thermogram of M2N (from Takimoto and Denault (45)).

The only instances where the product of reaction has an infrared spectrum almost identical to an infrared spectrum of a saturated solution of UN in UDMH, are reported by Mayer, Taylor and Schieler (47) and by Seamans and Dawson (46). Mayer and coworkers (47) obtained their product by reacting 50 μ l of UDMH with NO_2 vapor at 30 mm, and -11°C . The latter product was produced in a reaction at 25°C between UDMH vapor at 5 mm and NO_2 vapor at 5 mm.

UN can be prepared by the reaction of UDMH with nitric acid in dilute solutions and at low temperatures. As seen above, it also forms in a reaction between UDMH and N_2O , but is very sensitive to temperature and impurities.

Preparation and Properties

Considerable difficulty was encountered in preparing large batches of UN, primarily because it reverted to ammonium nitrate at some stage in the process. However, by carefully controlling the technique and reaction temperature, as well as the dilution, small quantities of UN were prepared in sufficient quantities to measure most of its properties.

UN was prepared in the same manner as MN, by combining concentrated nitric acid and UDMH in an ethanol solution at -20° to -30°C . UN, like the other fuel nitrates, is hygroscopic and special precautions must always be followed in order to avoid water contamination. A chemical analysis of the material, using the nitron technique (3), showed the salt to have a purity higher than 99 pct. Because of the hygroscopic nature of the material, considerable difficulty was experienced in preparing a good sample and in obtaining a satisfactory x-ray spectrum of UN. [The peaks that appeared in the densitometer tracings of the resultant films were not sharp triangles, as is usually the case, but short broad figures with irregular plateaus at the top. Locating the centers was difficult and the I/I_0 values were obtained by comparing areas instead of peak heights.] Table 11 shows the x-ray lines of the best spectrum. Infrared spectroscopic analysis of UN was obtained using the potassium bromide pellet technique; the spectrum is shown in figure 46. The infrared spectrum of a dilute solution of UN in UDMH is shown in figure 47.

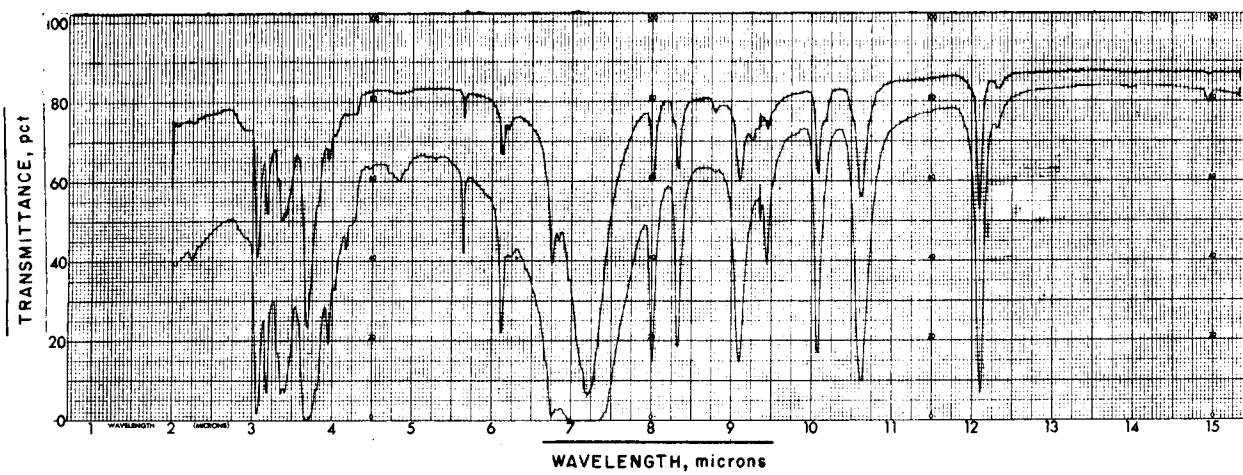


FIGURE 46. - Infrared Spectrum of UN.

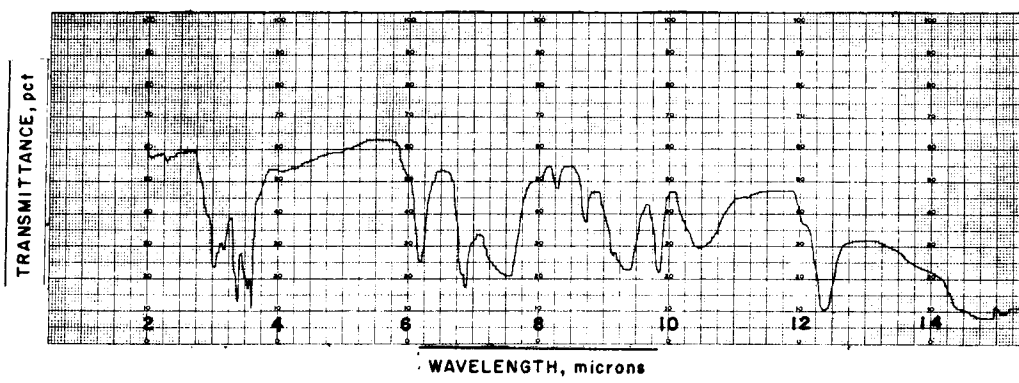


FIGURE 47. - Infrared Spectrum of a Dilute Solution of UN in UDMH.

TABLE 11. - X-ray diffraction spectrum of UN

d, Å	I/I ₀	d, Å	I/I ₀
7.11	10.4	2.80	15.1
5.86	10.3	2.64	28.4
5.32	28.5	2.51	1.9
5.07	6.1	2.42	9.2
4.86	6.0	2.36	2.0
4.60	41.9	2.26	3.6
4.38	100.0	2.18	2.6
3.86	49.9	2.10	5.4
3.63	5.2	1.89	1.8
3.54	28.7	1.84	6.0
3.40	1.2	1.81	2.3
3.29	35.9	1.76	2.7
3.12	22.5	1.70	3.8
2.91	9.3	1.65	4.3

Differential scanning calorimetry studies of UN showed a melting point of 43.5° C; it boiled at 153.5° C. On further heating, decomposition occurred at about 245° C. Although the decomposition occurred rapidly, it did not appear to be explosive. The TNT equivalence and shock sensitivity of UN were measured in the same manner as HN. Its TNT equivalence was measured to be 106 pct and its impact sensitivity, as measured by the ERL type 12 tool test (22)--which indicates a 50-pct probability of ignition--was 166 Kg-cm; thus UN is more sensitive to impact than is HN. References to UN or its properties were not found in the general literature.

TETRAMETHYLTETRAZENE (TMT)

Introduction

Among the reaction products of gaseous UDMH and gaseous NTO in the gas flow reactor studies (volume IV) was tetramethyltetrazene (TMT), believed to be one of the oxidation products formed in the engine residue from the UDMH portion of the A-50 fuel. In view of the triple nitrogen bond structure, one would surmise that this material might be an explosive substance. For this reason, some of its physical and combustion characteristics were studied by the Bureau.

Physical Characteristics

TMT was prepared according to a method described by Bull, Seaton and Audrieth (49) in which UDMH was oxidized by mercuric oxide. No particular difficulties were experienced in the preparation of this material and melting point measurements indicated it to be of high purity.

An infrared spectrum of liquid TMT was obtained and this is shown in figure 48; the spectrum is identical with that published in the literature (50).

The thermal decomposition of TMT was studied by Gowenlock, Jones and Snelling (51). They reported that over the temperature range of 193° to 260° C, the only products of decomposition observed were tetramethylhydrazine and nitrogen; while at temperatures above 260° C, trimethylamine and tetramethylmethylenediamine were formed. None of the decomposition products, however, represent a particular explosion hazard.

Mass spectroscopic data also were obtained and these are shown in table 12. Mass peaks at 59 and 102, corresponding to trimethylamine and tetramethylmethylenediamine, respectively, can be seen but they constitute very small quantities.

TABLE 12. - Mass spectrum of TMT¹

Mass	P.S.	Mass	P.S.	Mass	P.S.
2	37.0	42	2,230.0	62	4.4
12	79.0	43	1,830.0	63	8.0
14	500.0	44	1,930.0	64	2.6
15	1,680.0	45	690.0	65	9.4
16	36.6	46	37.0	66	2.8
17	29.5	50	6.8	67	1.6
18	² 800.0	51	8.1	68	1.8
28	2,260.0	52	3.6	69	4.0
29	93.0	53	2.0	70	8.1
30	149.0	54	2.8	71	8.1
31	8.5	55	5.7	72	207.0
32	17.7	56	6.0	73	17.0
37	3.7	57	12.8	74	1.7
38	120.0	58	45.0	116	520.0
39	172.0	59	127.0	117	33.3
40	372.0	60	4.0		
41	450.0	61	2.6		

¹Mass numbers 19 to 27 all gave bad peaks. Mass numbers 88 to 102 gave some peaks that may be due to the presence of (1) mercury traces, and (2) traces of the previous sample analyzed in the spectrometer.

²Bad peak.

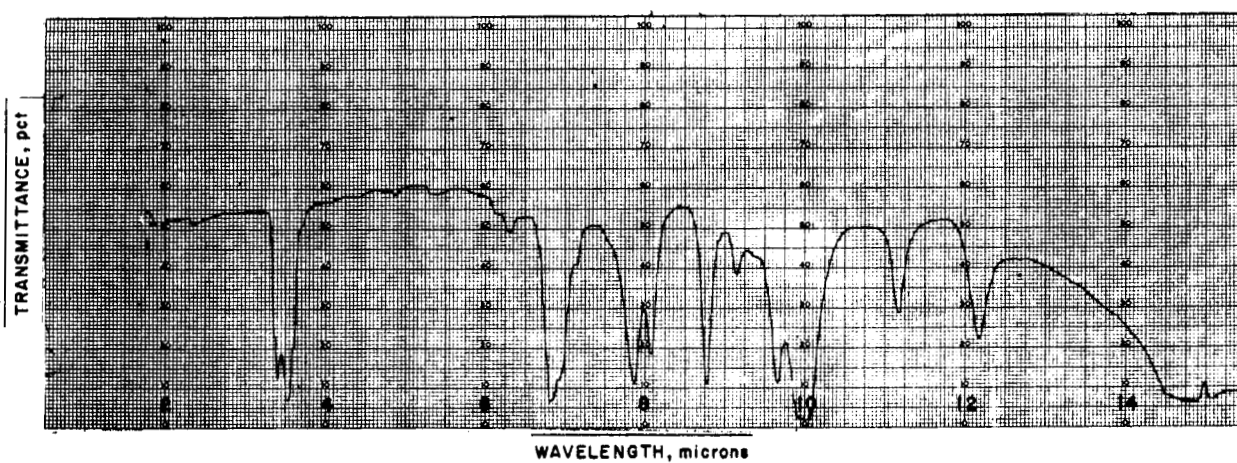


FIGURE 48. - Infrared Spectrum of Liquid TMT.

Explosion Characteristics

In view of the fact that TMT probably constitutes only a small fraction of the engine residues, only its TNT equivalence and impact sensitivity were determined. Following the same procedure as used for HN, a TNT equivalence of 50.5 was obtained. In the impact experiments, TMT did not detonate, even at the maximum impact condition of 1,500 Kg-cm available with the Bureau apparatus.

HYDRAZINE AZIDE

Introduction

Azides were among the explosive materials initially suggested as possible constituents of the engine residues (52). Hydrogen azide, specifically, is a very powerful and extremely sensitive explosive. There is much evidence of its great sensitivity to light, impact, and heat, among other initiating sources. There is the possibility of hydrazine azide forming in the engine. The engine is known to contain both N_2H_4 and the azide ion, N_3^- , in addition to hydrogen azide. The azide ion was found in the infrared spectra of the reaction between N_2H_4 and NTO at low temperatures (52-53). The azide group has also subsequently been found in the spectra of both the Bureau's flow reactor and 2-D plastic engine reaction products. Although it is usually present in quite small amounts, there were a few instances in which the concentration was observed to be dangerously high. The instability of azides originates from the triple nitrogen configuration. Even small amounts of hydrogen azide (17 pct by weight) dissolved in water have been observed to constitute an explosive mixture (54).

Preparation and Physical Characteristics

Hydrazine azide was prepared according to a method described in U.S. patent No. 3,155,456 (55) in which the azide is formed by the reaction of sodium azide, hydrazine, and hydrazine sulfate. This mixture was refluxed in a 2-liter n-butanol solution for 15 min at 170° C, following which the solvent was decanted, cooled to a temperature of ~5° C, whereupon a crystalline product separated out. This material was filtered, washed with ether, and dried. It was analyzed by procedures described in Milspecs MIL-P-27402 (U.S. Air Force) (56) and its purity was calculated to be greater than 98.5 pct.

A separate quantitative test for azides also was conducted and these results substantiated this analysis. Both infrared and x-ray spectra were obtained for this material. The infrared spectrum is shown in figure 49. Because of the very hygroscopic nature of hydrazine azide, considerable difficulty was experienced in obtaining a satisfactory sample for x-ray spectral analysis. The values obtained are shown in table 13.

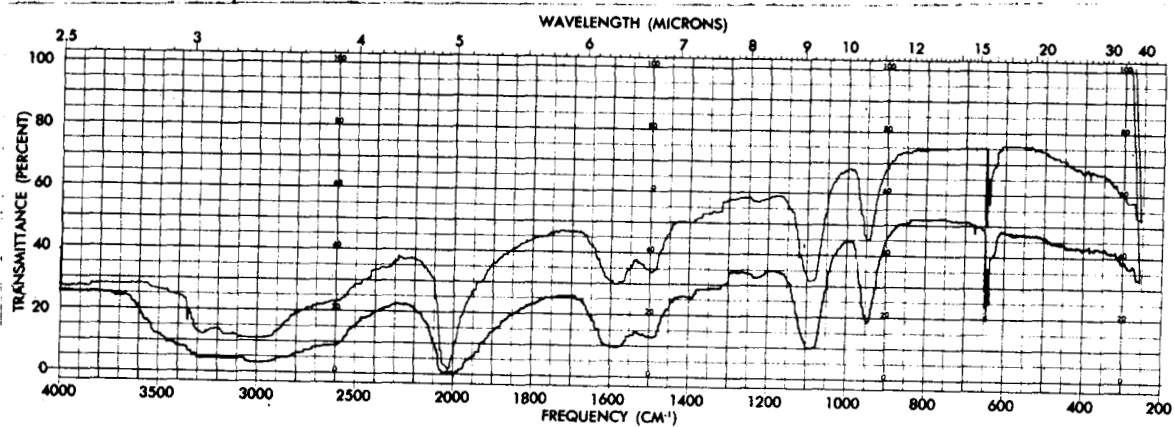


FIGURE 49. - Infrared Spectrum of Hydrazine Azide.

TABLE 13. - X-ray diffraction spectrum
of hydrazine azide

$d, \text{\AA}$	I/I_0
5.80	1.0
5.12	2.8
3.35	78.7
3.23	100.0
2.87	61.1
2.71	6.5
2.54	25.5
2.46	2.4
2.32	2.8
2.28	9.7
2.18	3.0
2.12	5.4
2.08	9.2
1.85	5.4
1.74	6.9
1.57	4.4
1.55	4.1
1.52	4.6
1.49	5.9

A thermal analysis in the DSC was performed; the melting point and boiling point were found to depend strongly on the heating rates used during the analysis. Although this phenomenon has been known and has been mentioned earlier in this volume, the degree of dependency on heating rate varies from material to material, and is affected by such factors as sample size and crystal size. For the hydrazine azide, the melting point varied between 59° and 67° C and the boiling point varied between 79° and 93° C.

Combustion Characteristics

The TNT equivalence and impact sensitivity of hydrazine azide were measured in the same manner as used for the HN. The TNT equivalence was 144 pct and the impact sensitivity, using the cup-and-plunger technique, 815 Kg-cm.

NITROSYL AZIDE

Although never actually observed in the spectra of engine residues, nitrosyl azide is suspected of being a short-lived, intermediate product in the engines, and because of its highly reactive and unreliably explosive nature, some consideration was given to this material.

It is known to form according to the following reaction:



and both hydrogen azide and nitrous acid are believed to be present in the engine during engine operation.

Although the Bureau did not prepare this substance, other researchers (57) have prepared it and some of its characteristics have been measured.

Nitrosyl azide is a yellow liquid freezing between -66°C and -55°C , depending upon the method of preparation; its extrapolated boiling point is in the vicinity of 1°C . It has the chemical formula N_4O , and as one might suspect from such a molecular structure, the material is extremely unstable. The two characteristics of this material which attracted our attention were the nearness of its melting point, -66°C , to the temperature at which frozen N_2H_4 and NTO have been observed to react violently, and the nitrosyl ion two prominent absorption bands in the infrared, one at 4.28μ and one at 5.4μ , both of which were observed in the infrared spectra of the reaction between N_2H_4 and NTO, at the low temperature range of -133° to -124°C (53). These observations lead one to suspect that the nitrosyl azide may be the unstable low-temperature reaction product of the reaction between N_2H_4 and NTO at -133°C . Certainly, more work needs to be done before this observation can be verified.

SUMMARY

It has been established that the physical characteristics of the engine residues as well as their combustion characteristics are significant in establishing explosion hazards within these RCS engines. The residue viscosity and surface tension play a major role in the formation of deposits of these materials necessary to constitute explosive systems. After having measured the viscosity and surface tension for hydrazine nitrate solutions in both water and hydrazine, one can then estimate the nature of the deposits under various engine operating conditions.

It also has been established that hydrazine nitrate does not thermally dissociate sufficiently rapidly below its explosion decomposition limit to provide a means for removal of this material by heating the engine and removing the HN faster than it is being formed. Thin film detonation studies have demonstrated that relatively thin films of HN/H₂H₄ solutions can be detonated when suitably initiated. Although the detonation of the film per se does not probably destroy an engine, the gas pressure resulting from the explosion can. Impact sensitivity studies indicate that HN is not particularly sensitive. Although it was demonstrated that these films can detonate in situ, it was subsequently shown that the combustible material deposited on the engine walls is explosively burned after removal from the wall by a heterogeneous detonation in the gas-phase. Although the presence of a low velocity detonation in the thin film studies suggested the possibility of cavitationally induced detonation initiation, no evidence was found to indicate that cavitated HN/N₂H₄ solutions are shock sensitive.

Additional studies also were conducted on hydrazine dinitrate, hydrazine nitrite, monomethylhydrazine nitrate, unsymmetrical dimethylhydrazine nitrate, tetramethyltetrazene, hydrazine azide, and nitrosyl azide. Unfortunately, time did not permit a thorough investigation of all the physical and combustion characteristics. However, it was concluded that none of these materials individually represent a particularly hazardous material contrary to many original suggestions. It is conceivable that mixtures of these materials may significantly increase the explosion hazard.

REFERENCES¹²

1. Curtius, T., and R. Jay. Diazo-und Azoverbindungen Der Fettreihe. IV. Abhandlung Ueber Das Hydrazin. (Diazo and Azo Combinations of the Aliphatic Series. IV. Treatise on Hydrazine). J. Prakt. Chemie., v. 147, 1889, p. 27.
2. Thiokol Corp. Rept. RMD-239-Q1 (period June-September 1958), Contract No. as 58-644 C.
3. Furman, N. H., editor. Scott's Standard Methods of Chemical Analysis. D. Van Nostrand, New York, 5th ed., v. 1, 1939, p. 635.
4. Robinson, R. J., and W. C. McCrone. Hydrazine Nitrate (1). Anal. Chem., v. 30, 1958, pp. 1014-1015.
5. Sommer, Fritz. Studien über das Hydrazin und Seine Anorganischen Derivate. (Studies on Hydrazine and its Inorganic Derivatives. II. Monotropism of Hydrazine Nitrate). Z. Anorg. Chemie, v. 86, No. 1, February 27, 1914, pp. 71-86.
6. Medard, Louis. Propriétés Explosives Du Nitrate D'Hydrazine. (Explosive Properties of Hydrazine Nitrate). Mémorial des Poudres, v. 34, 1952, pp. 147-157.
7. Kissinger, L. W. The Preparation and Properties of Hydrazine Mononitrate, U.S. Naval Ordnance Lab., Memo 10,359, July 7, 1949, 4 pp.
8. Sabanejeff, A. Über einige anorganische Hydrazinsalze und über die Darstellung der Stickstoffwasserstoffsäure. (Some Inorganic Hydrazine Salts and the Preparation of Hydrazoic Acid). Zeitschrift für Anorganische Chemie, v. 20, No. 1, March 1899, pp. 21-29.
9. Cook, M. A., and M. Taylor Abegg. Isothermal Decomposition of Explosives. Ind. and Eng. Chem., v. 48, 1956, pp. 1090-1095.
10. Vango, S. P., and J. B. Krasinsky. Density, Vapor Pressure, and Viscosity of Solutions of Hydrazine Mononitrate in Hydrazine. Jet Propulsion Lab., Calif. Inst. of Technol., Pasadena, Calif., Tech. Memo. 33-103, October 15, 1962, 12 pp.
11. Clark, C. C. Hydrazine. Mathieson Chemical Corp., Baltimore, Md., 1953, pp. 19-29.
12. Lange, N. A., editor. Handbook of Chemistry. Handbook Publishers Inc., Sandusky, Ohio, 5th ed., 1944.

¹²Titles enclosed in parentheses are translations from the language in which the item was published.

13. Partington, J. R. An Advanced Treatise of Physical Chemistry: The Properties of Liquids. Longmans, Green and Co., New York, v. 2, 1951, p. 185.
14. Elverum, G. W., Jr., and L. G. Cole. Some Physical-Chemical Studies of the System Hydrazine-Hydrazine Nitrate-Water. Jet Propulsion Lab., Calif. Inst. of Technol., Pasadena, Calif., Memo. 20-79, December 30, 1952, 13 pp.
15. Corcoran, J. M., H. W. Kruse, S. Skolnik, and E. Lieber. Thermal Analysis of the System Hydrazine Nitrate-Water-Hydrazine. U.S. Naval Ordnance Test Station, Inyokern, China Lake, Calif., NAVORD Rept. 2087, January 26, 1954, 13 pp.
16. Rosen, J. M. A New Apparatus for the Determination of the Ignition Temperature of Explosives. U.S. Naval Ordnance Lab., Memo 10,289, December 21, 1949, 21 pp.
17. Crow, E. L., F. A. Davis, and M. W. Maxfield. Statistics Manual. Dover Publications Inc., New York, 1960, p. 93.
18. Shidlovskii, A. A., V. I. Semishin, and V. I. Simutin. (Thermal Decomposition and Combustion of Hydrazine Nitrate). J. Applied Chem. (U.S.S.R.), v. 33, No. 6, 1960, pp. 1411-1413.
19. Levy, J. B., G. von Elbe, R. Friedman, T. Wallin, and S. J. Adams. The Deflagration of Hydrazine Perchlorate. Advanced Propellant Chem., ed. by R. F. Gould. American Chem. Soc., New York, 1966, p. 63.
20. Price, D., T. P. Liddiard, Jr., and R. D. Drosd. The Detonation Behavior of Hydrazine Mononitrate. U.S. Naval Ordnance Lab., Rept. NOLTR-66-31, April 15, 1966, 15 pp.
21. Clairmont, A. R., Jr., I. Jaffe, and D. Price. The Detonation Behavior of Ammonium Perchlorate as a Function of Charge Density and Diameter. U.S. Naval Ordnance Lab., Rept. NOLTR-67-71, June 20, 1967, 43 pp.
22. Eyster, E. H., and L. C. Smith. Studies of the ERL Type 12 Drop-Weight Impact Machine at NOL. U.S. Naval Ordnance Lab., Memo. 10,003, January 25, 1949, 29 pp.
23. Smith, L. C., and S. R. Walton. Miscellaneous Physical Testing of Explosives. U.S. Naval Ordnance Lab., Memo. 10,381, September 21, 1949, 9 pp.
24. Seamans, T. F., and B. E. Dawson. Hypergolic Ignition at Reduced Pressures. AFRPL-TR-67-129, June 1967, 125 pp.

25. Hodgkinson, W. R. E. Some Reactions of Hydrazine Nitrate. J. Soc. Chem. Ind., v. 32, 1913, pp. 519-520.
26. Ribovich, J. A Wedge Technique for Evaluation of Detonation Hazards of Liquid Explosives. Ann. Acad. Sci., New York, v. 152, art. 1, October 28, 1968, pp. 766-772.
27. Wiebenson, W. E., Jr., W. H. Zwisler, L. B. Seely, and S. R. Brinkley, Jr. TIGER Computer Program Documentation I. Theoretical and Mathematical Formulations for the Tiger Computer Program. Prepared for Ballistic Res. Lab., Aberdeen, Md., as part of U.S. Army Explosive Research Program under contract No. DA-04-200-AMC-3226 (X), November 1968.
28. Dwiggins, R. D., and B. F. Larrick. Investigation of Mixtures of Hydrazine, Hydrazine Nitrate, and Water. Part II. Progress Report covering the period from April 1 to June 30, 1952. U.S. Naval Ordnance Lab., Rept. 2563, August 13, 1952, 15 pp.
29. Audrieth and Mohr, unpublished work, University of Illinois. Reference to this work appears in The Chemistry of Hydrazine, L. F. Audrieth and B. A. Ogg. John Wiley & Sons, Inc., New York, 1951.
30. Welsh, T. W. B., and H. J. Broderson. Anhydrous Hydrazine. IV. Chemical Reactions in Anhydrous Hydrazine. J. Am. Chem. Soc., v. 37, 1915, pp. 825-832.
31. Gibson, F. C., M. L. Bowser, C. R. Summers, and F. H. Scott. An Electrical Method for the Continuous Measurement of Propagation Velocities in Explosives and Propellants. BuMines RI 6207, 1963, 8 pp.
32. Watson, R. A. Gauge for Determining Shock Pressures. Review of Scientific Instruments, v. 38, No. 7, July 1967, pp. 978-980.
33. Christos, T., Y. Miron, H. James, and H. E. Perlee. Exploratory Study of Hypergolic Ignition Spike Phenomena, Part II, Phase II. Order No. T-39882 (G). Manned Spacecraft Center, Houston, Tex., July 1 to September 30, 1966, 14 pp.
34. Watson, R. W., C. R. Summers, F. C. Gibson, and R. W. Van Dolah. Detonations in Liquid Explosives--The Low-Velocity Regime. Proc. Fourth Symp. (Internat.) on Detonation. ACR-126. U.S. Naval Ordnance Lab., White Oak, Md. Office of Naval Research, Dept. of the Navy, October 12-15, 1965, pp. 117-125.

C-2

35. Zeleznik, F. J., and S. Gordon. A General IBM 704 or 7090 Computer Program for Computation of Chemical Equilibrium Compositions, Rocket Performance, and Chapman-Jouguet Detonations. NASA TN D-1454. Lewis Res. Cen., Cleveland, Ohio, October 1962.
36. Loison, R. The Propagation of Deflagration in a Tube Covered with an Oil Film. *Comptes Rendues*, v. 234, No. 5, Paris, France, 1952.
37. Ragland, K. W., E. K. Dabora, and J. A. Nicholls. Shock Induced Heterogeneous Detonations. Paper pres. at the 1965 fall mtg. of Western States Section of the Combustion Inst., WSCI 65-22, October 1965.
38. Gordeev, V. E., V. F. Komov, and Y. K. Troskin. Concerning Detonation Combustion in Heterogeneous Systems. *Proc. Acad. of Sci., U.S.S.R., Phys. Chem.*, v. 160, No. 4, 1965.
39. Borisov, A. A., S. M. Kogarko, and A. V. Lyubimov. Ignition of Fuel Films Behind Shock Waves in Air and Oxygen. *Combustion and Flame*, v. 12, October 1968, pp. 465-468.
40. Rybanin, S. S. A Unidimensional Model for Detonation in Heterogenous Systems. *Doklady Akademii Nauk, U.S.S.R.*, v. 168, No. 4, June 1966, pp. 857-859.
41. Pimentel, G. C., S. W. Charles, and K. Rosengren. Hydrogen Bonding of Hydrazoic Acid in Solid Nitrogen. *J. Chem. Phys.*, v. 44, No. 8, 1966, pp. 3029-3033.
42. Mellor, J. W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Longmans, Green and Co., New York, v. VIII, 1928, pp. 472-473.
43. Audrieth, L. F. Parallelism in the Decomposition of Ammonium, Hydrazine, and Hydroxylammonium Nitrites. *J. Phys. Chem.*, v. 34, 1930, pp. 538-542.
44. Sommer, Fritz. Studien über das Hydrazin und Seine Anorganischen Derivate. I. Über Hydrazinnitrite und ihre Zersetzungsprodukte. (Studies on Hydrazine and its Inorganic Derivatives. I. Hydrazine Nitrite and its Decomposition Products). *Zhurnal Anorganische Chemie*, v. 83, No. 2, October 2, 1913, pp. 119-137.
45. Takimoto, H. H., and G. C. Denault. Combustion Residues from N_2O_4 -MMH Motors. Aerospace Corp. Rept. No. TR-0066(5210-10)-1, September 15, 1969.
46. Seamans, T. F., and B. E. Dawson. Hypergolic Ignition at Reduced Pressures. Thiokol Chemical Corp., Rept. RMD 5809-01, 1966.

47. Mayer, S. W., D. Taylor, and L. Schieler. Preignition Products from Storable Propellants at Simulated High Altitude Conditions. Aerospace Corp. Rept., TR-0158(9210-02)-1, November 1967.
48. Zung, L. B., and B. P. Breen. A Basic Study on the Ignition of Hypergolic Liquid Propellants. Dynamic Science, 3d Quarterly Rept. NAS 7-438, Mod. No. 6, February 20, 1969.
49. Bull, W. E., J. A. Seaton, and L. F. Audrieth. Some Properties of Tetraalkyl-2-Tetrazenes. J. Am. Chem. Soc., v. 80, 1958, pp. 2516-2518.
50. Pierson, R. H., A. N. Fletcher, and E. St. Clair Gantz. Catalog of Infrared Spectra for Qualitative Analysis of Gases. Anal. Chem., v. 28, No. 8, August 1956, pp. 1218-1239.
51. Gowenlock, B. G., P. P. Jones, and D. R. Snelling. The Thermal Decomposition of Tetramethyltetrazene and Tetraethyltetrazene. Can. J. Chem., v. 41, 1963, pp. 1911-1918.
52. Ray, A. B., G. Koehler, G. E. Salser, and L. Dauerman. Chemical Intermediates Responsible for Pressure Spikes in Engines using Nitrogen Tetroxide and Hydrazine. Personal communication.
53. Weiss, H. G. A Basic Study of the Nitrogen Tetroxide-Hydrazine Reaction. Dynamic Science Corp., Monrovia, Calif. Rept. No. SN-4500, JPL (contract No. BE4-229751), NASA (subcontract No. NAS 7-100), July 1965.
54. Taylor, J. Detonation in Condensed Explosives, Oxford at the Clarendon Press, 1952, p. 158.
55. Henderson, U. V., Jr., and W. G. Courtney. Process of Preparing Hydrazinium Azide. U.S. Patent No. 3,155,456. Richmond, Va., assigns to Texaco Experiment Inc.
56. Military Specifications. MIL-P-27402 (USAF).
57. Lucien, H. W. The Preparation and Properties of Nitrosyl Azide. J. Am. Chem. Soc., v. 8, 1958, pp. 4458-4460.